

United Aircraft Research Laboratories



Investigation of the Kinetics of
Crystallization of Molten Binary
and Ternary Oxide Systems

Summary Report and Quarterly Status Report No. 4

Contract NASW-1301

REPORTED BY James F. Bacon
J. F. Bacon

APPROVED BY R. Fanti
R. Fanti, Chief
Materials Sciences

DATE September 30, 1966

NO. OF PAGES 61

COPY NO. _____

Investigation of the Kinetics of Crystallization of

Molten Binary and Ternary Oxide Systems

Summary and Quarterly Status Report No. 4

TABLE OF CONTENTS

| | <u>Page</u> |
|--|-------------|
| SUMMARY | i |
| INTRODUCTION | 1 |
| PREPARATION OF GLASS SYSTEMS FOR PRELIMINARY EVALUATION | 1 |
| PROCEDURES FOR CHARACTERIZING GLASS SYSTEMS INVESTIGATED AND THE RESULTS OBTAINED | 5 |
| Electrical Conductivity Measurements | 6 |
| Viscosity Measurements | 7 |
| Elastic Modulus Measurements | 9 |
| Evaluation of Glass Forming Characteristics and Fiberizability . . | 14 |
| CONCLUSIONS | 15 |
| PERSONNEL ACTIVE ON PROGRAM | 15 |
| REFERENCES | 16 |
| TABLES I - X | 21 |
| FIGURES 1 - 18 | 44 |

Investigation of the Kinetics of Crystallization of

Molten Binary and Ternary Oxide Systems

Summary and Quarterly Status Report No. 4 - June 1, 1966 through August 31, 1966

Contract No. NASW-1301

SUMMARY

In the first year of this contract ninety-six mixtures of oxides were studied comprising eighty distinct compositions belonging to nine different glass systems not previously studied in connection with glass fiber research. Throughout the program emphasis has been placed on systems likely to form complex three-dimensional structures with higher than usual values of elastic moduli. Systems studied included cordierite glasses with nucleating and anti-nucleating additives, the benitoite and beryl systems to a very limited extent, fluoborate glasses, Morey's tantalum oxide-titania-lanthanum borate (no silica) glasses, and "invert" glasses.

Concurrently with the molten oxide composition research, equipment necessary to carry out an adequate characterization of such glasses was assembled, viscosities at temperature were measured for sixteen glasses with a standard model Brookfield viscometer fitted with elongated tungsten shaft and spindle and calibrated at or nearly at room temperature by use of N.B.S. standard viscosity oil "P" and a constant temperature water-bath. Electrical conductivity measurements were made from 860 C to 1560 C using a tungsten conductivity cell and selected circuitry. Sonic measurements of Young's modulus for twenty-four glasses were made with satisfactory precision using circuitry built in this laboratory and these measurements were corroborated using the conventional stress-strain curve, beam deflection technique. Fiberizability studies were made on twenty-seven of the compositions and demonstrated the ease with which most of the compositions tested could be used for glass fiber production. Finally equipment was assembled to permit the dynamic measurement of the shear modulus for the various oxide melts studied so that in conjunction with the determination of Young's modulus, an estimate of the anisotropy of glasses produced can be made.

At this time the best glasses developed show consistently an average value for Young's modulus above fifteen million psi for samples of bulk glass without any special heat treatment. This is a higher value than that obtained by most prior contractors but is lower than the eighteen to twenty-one million psi postulated as a goal for this program. That such a goal may be readily obtainable by further refinements of this program is indicated by the fact that occasional glass samples were produced with values for Young's modulus for the bulk glass above seventeen and a half million psi. Not all of the glasses already prepared have been characterized as yet and this work will be continued in the extended contractual period together with research on additional molten oxide mixtures with much stronger emphasis on the determination of the kinetics of crystallization of such mixtures.

INTRODUCTION

This is the fourth quarterly status report as well as the first summary report for Contract NASW-1301 entitled, "Investigation of the Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems." The fourth quarter of the contract started June 1, 1966 and extended to August 31, 1966 while the period summarized started September 1, 1965 and extended likewise to August 31, 1966. The primary objective of this program is to gain a better understanding of the essentials of glass formation by measuring the rate at which crystallization occurs and the effects of anti-nucleating agents on the observed crystallization rate for systems which tend to form complex three dimensional structures. Determination of the crystallization rate is carried out by continuously measuring the viscosity and electrical conductivity of the molten system as a function of time and temperature with checks of surface tension at selected temperatures. Glass formation in this research is, therefore, regarded as a rate phenomenon where the probability of such glass formation is greatly increased by employing cooling rates high enough to defeat the formation of the complex many-atom three-dimensional molecule. This view of glass formation justifies the consideration of oxide systems previously thought impractical and allows the search for systems which may yield high strength, high modulus glass fibers to be carried out on an unusually broad basis.

PREPARATION OF GLASS SYSTEMS FOR PRELIMINARY EVALUATION

Progress has been made in several areas in the twelve months of the contract period. Reports from programs previously sponsored by the Government in the area of glass fiber research together with the published literature in this field appearing in the last ten years have been reviewed. Examination of the many Government-sponsored research contracts in this area (Refs. 1 through 39) has shown that although several thousand glass compositions have been melted in an effort to produce improved glass fibers no conflict exists with the directions of research planned by UACRL. Only one other contractor, Refs. 14 through 17, has been concerned with structured glasses and this contractor has largely concentrated on patterning glasses after those materials exhibiting an infinite linear chain structure such as asbestos, the pyroxenes, the amphiboles, the diopsides, and the spodumenes. The hope of this research was that by forming glass fibers from glass melts which have linearly orientable groupings of atoms, this orientation would persist in the molten state and would, therefore, yield an oriented or anisotropic glass fiber of high strength and modulus. It can be seen, accordingly, that the theoretical considerations motivating these investigators as well as their choice of structures to be investigated (Refs. 14 through 17) are distinct when compared to the current investigation.

However, toward the end of the first contractual period these investigators did include the cordierite glass field composition as the only ring-type silicate structure (glass composition C-7, pg. 45, Ref. 16) investigated and found it to be difficultly fiberizable (pg. 46) but did not otherwise characterize it because of time limitations (pg. 51). No mention is made (Refs. 14 through 17) of the other ring-type silicate structures studied in the current investigation.

The first oxide system to be selected for investigation, cordierite or $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ --a three-dimensional ring former, has been melted successfully on fourteen occasions (Table IA and footnote) in several atmospheres and in several containers. Typically these glasses are prepared in 500 gram batches in high purity (99.9%) alumina crucibles in air in the super-kanthal hair-pin kiln shown in Fig. 1. Starting materials used are 5 micron particle size, high purity silica, high purity alumina of 325 mesh, and laboratory reagent grade basic magnesium carbonate. These materials yield a water-white optical grade glass free of seed, stone, and bubbles when held at a temperature of 1540 C or higher for at least two hours. Less commonly the glass has been prepared in beryllia crucibles in air and in the kiln or in platinum or tungsten crucibles in purified argon or in vacuum in the tungsten resistance furnace of Fig. 3. Alumina crucibles of even slightly lower purity, i.e., 99.3 to 99.7% cannot be used nor can the temperature of 1540 to 1560 C be exceeded even with the highest purity alumina crucible.

Equipment developed for monitoring the electrical conductivity of the molten oxide system as it cools has been used successfully to measure the electrical conductivity of the vitreous cordierite system from 1560 C to 860 C as described in the following sections. Apparatus put together to carry out the dynamic measurement of Young's modulus of the bulk glass has consistently yielded an elastic modulus 50% higher than the usual commercial glasses such as fused silica or C.G.W. 7740 as well as yielding experimentally an elastic modulus 10% higher than that calculated using the method of C. J. Phillips (Ref. 40). This glass system seemed ideal for further experimentation and, therefore, the seventeen batches based on this system and listed in Table IA were prepared by adding nucleating and anti-nucleating agents to the system. Evaluation of these new glasses is still in progress but the preliminary data obtained on some of them is shown in Tables IV, V, VI, and X. The results continue to appear promising but obviously much further research is required for a definite conclusion.

Douglas (Ref. 46) recapitulates the Zachariasen rules relating the probability of a glass formation to the structure of the crystalline form of the material as:

1. An oxygen atom is linked to not more than two atoms, A;
2. A must be small;

3. The oxygen polyhedra share corners with each other, not edges or faces and form three-dimensional networks;
4. At least three corners in each oxygen polyhedra must be shared.

A large number of the glasses prepared in the third period of this report belong to novel glass systems developed by Stevels (Ref. 46) and called by him "invert" glasses. These glasses which may contain as little as 34 mol % silica and whose mechanical properties have never previously been studied as far as is known controvert Zachariassen's rules 3 and 4. The composition of these glasses is frequently indicated by a parameter Y designating the average number of bridging ions per SiO_4 tetrahedron and calculated from the expression

$$Y = 6 - \frac{200}{P} \quad \text{where } P = \text{Mol } \% \text{ SiO}_2$$

so that when $P = 33\frac{1}{3}$, $Y = 0$ and the SiO_4 groups are isolated; when $P = 40\%$, $Y = 1$ and on the average SiO_4 groups appear in pairs. Properties of these glasses such as the viscosity at a given temperature, the viscosity activation energy, thermal expansivity, electrical deformation loss go through extreme values when the parameter Y passes through the value of 2.0. There is every reason, therefore, to believe that mechanical properties such as Young's modulus will show a similar "parabolic" curve when plotted against the parameter Y climbing steeply as Y decreases from 2 to 1 to 0, but no prior experimental data is available to support this hypothesis.

With these considerations twenty-eight "invert" glasses were prepared in three series (Table IB). The three series were respectively silica-lead-mixed alkaline earths, silica-titania-mixed alkaline earths, silica-zirconia-mixed alkaline earths. While characterization of these glasses is not yet complete, three members of each series have been evaluated without any evidence of increased modulus. Many other series of "invert" glasses exist, however, and the negative results today may merely indicate that some other choice should be made.

A distinctly different type of non-silicate, non-alkali glass system not previously studied by glass fiber research scientists is that built on acid forming elements having relatively high atomic weights. These glasses due to Morey (Ref. 43) and improved for practical manufacture by DePaoli (Ref. 44) may be made, for example, from a mixture of titania and tantalum oxide or from tantalum oxide, zirconia and lanthana. They typically include no alkali and little or no silica and are, therefore, too refractory to be melted in conventional glass-fiber apparatus. Published data (Ref. 45) for similar glasses supports the idea that these glasses have elastic moduli higher than conventional glasses and lack of silica lends hope that such systems may not suffer atmospheric deterioration to the extent common with silicate based glasses. UACRL has melted these glasses

on nine occasions but has not succeeded in producing glass suitable for evaluation. Further attempts will be made in the next period. The compositions investigated during the first year are shown in Table IC.

Table ID summarizes the other types of molten oxide mixtures which have been studied during the first year. In general, these compositions have received much less emphasis than those mentioned above either because they have not yet been melted successfully or because their properties proved relatively uninteresting. They include a number of diverse systems however. For example, one of the types of glasses apparently not previously studied in connection with glass fiber formation is the fluoborate optical glass system (Refs. 41, 42). These glasses contain little or no alkali which according to Phillips calculations (Ref. 40) contributes to low elastic modulus and very little or no silica. Attempts have been made to melt the four compositions shown in Table ID⁴ but to date have failed because of excessive foaming.

A second ring structure which should be equally as promising as that of cordierite is benitoite, $\text{BaTiSi}_3\text{O}_9$, whose structure consists of ring ions arranged in sheets with their planes parallel with the metal ions falling between the sheets and binding together the rings of the different sheets. Although this system has now been experimented with on several occasions, Table ID⁶, no glass has as yet been prepared because of the speed of devitrification of the system in platinum or tungsten crucibles and because of inability to contain this molten oxide system in high purity alumina, magnesia, or beryllia crucibles. Further research will be attempted in the next year.

No attempt has yet been made to prepare glasses from oxide mixtures of such proportions that only beryl (emerald structure) a third silicate ring structure would result. However, three glasses have been melted where beryl should constitute the predominant crystalline phase, Table ID⁶. Two of these glasses were obtained as optical grade materials but as yet it has proven impossible to cool the third one fast enough to prevent devitrification. The better of the two glasses is about seven percent inferior compared to the worst cordierite glass and the other "beryl" glass is even less outstanding since it is almost impossible to fiberize. However, research on this system will continue as soon as new ventilation ducts are installed.

Later in the report, it is shown that calculations of Young's modulus from composition by the methods of Phillips (Ref. 40) indicate zirconia should be very effective in increasing the modulus. The six high zirconia glasses of Table ID¹ were consequently prepared but did not show any outstanding values for the elastic modulus.

For purposes of ascertaining the kinetics of crystallization of molten oxide systems, systems with either two or three oxides only (Table ID2 and ID3) would be much simpler to measure. However, no success has been obtained in attempting to prepare glasses from these systems and the cordierite systems of Table IA continue to be the simplest systems consistently melted at this stage of the investigation.

Finally a few miscellaneous oxide systems were prepared and shown in Table ID7 but these have not yet been evaluated at this time.

To summarize, therefore, ninety-six melts of more than eighty distinct compositions have been prepared and as will be shown the viscosities have been measured for sixteen of these systems, Young's modulus for twenty-four, and glass forming and fiberizability studies carried out for twenty-seven. Many further characterization studies are necessary.

PROCEDURES FOR CHARACTERIZING GLASS SYSTEMS INVESTIGATED AND THE RESULTS OBTAINED

The kinetics of crystallization of the glass systems investigated under this contract are to be determined from continuous measurement of the electrical resistivity and viscosity of the system together with spot checks at selected temperatures of the surface tension of the molten oxide systems. These measurements plus the measurement of Young's modulus of the bulk glass at room temperature serve to help characterize the system studied. In addition with the recently added equipment for measuring shear modulus and through it and Young's modulus, the ability to determine Poisson's Ratio the tools are at hand to decide whether any of the glasses formed remember their initial structure to the extent that they show anisotropy after melting. Finally, characterization of the molten oxide systems is completed by determination of their glass forming and fiberization qualities.

In this section of the report the equipment used for electrical conductivity studies, for viscosity measurements, for the determination of Young's modulus and the shear modulus, and for studying fiberizability are discussed in detail and the results obtained during the first year of the contract with this equipment are tabulated.

Electrical Conductivity Measurements

To study the electrical conductivity of the molten oxides as a function of time and temperature, the glasses were melted as described above and broken up and packed into the tungsten crucible shown in Fig. 2. This crucible, which is pictured at the conclusion of the measurement, is made to serve as a conductivity cell by introducing a tungsten ball, one-quarter inch in diameter, on the end of a tungsten rod into the exact center of the crucible and by tying a tungsten rod to the outside of the crucible with 25 mil tantalum wire. The whole assembly is then placed in the tungsten resistance furnace shown in Fig. 3 and heated until the glass is completely remelted. Power to the furnace is then turned off and the electrical conductivity of the molten oxide system is measured continuously through the solidification process as the furnace cools. The temperature of the crucible is measured at thirty-second intervals to obtain the required data connecting electrical conductivity with crystallization or lack of crystallization rates.

The actual measurement of the electrical conductivity is carried out by connecting externally the UACRL "log ohmmeter" described schematically in Fig. 4 to the two leads from the tungsten crucible conductivity cell. These leads are brought out of the furnace using vacuum-type electrical lead-ins. The log ohmmeter of Fig. 4 is designed to measure resistance from 10^{-1} ohms to 10^{+6} ohms and generates a d-c signal voltage proportional to the logarithm of the resistance. The scale for this instrument is divided into six ranges: 10^{+6} ohms to 10^{+5} ohms, 10^{+5} to 10^{+3} ohms, 10^{+3} to 10^{+2} ohms, 10^{+2} ohms to 10 ohms, 10 ohms to 1 ohm, and 1 ohm to 10^{-1} ohm. Over each range, the amplitude of the signal applied to the unknown resistor and the sampling resistor are adjusted so that the power dissipated in the sample is less than 500 microwatts, and the sample resistor is less than 6.5 percent of the resistance being measured.

In each range position, a constant amplitude, 1000 cycle/sec, sinusoidal voltage is applied to the unknown and the current through it measured by a sampling resistor. This signal is passed through a series of filters consisting of a band-pass filter from 800 to 2000 cycles/sec, a twin-tee notch filter at 60 cycles/sec and a twin-tee notch filter at 180 cycles/sec in cascade. These filters effectively remove the large amount of noise generated in the sample by the massive (1000's of amperes) 60 cycle heater current present in the tungsten furnace. The signal is then linearly amplified by a guarded amplifier to a level of 0.5 volts p-p to 50 volts p-p and used to drive a power amplifier. The power amplifier isolates the guarded amplifier from the detector. The d-c voltage from the detector is then applied to the logarithmic converter which puts out a d-c voltage proportional to the logarithm of the input voltage. A unity gain operational amplifier following the logarithmic converter provides the low output impedance necessary to drive the strip chart recorder.

The electrical conductivity device has been used successfully for several of the molten oxide systems. However, the measurements did not seem as useful in selecting those molten oxide systems for further study as did direct measurements of viscosity, elastic moduli, and fiberizability. Attention has been concentrated on these latter measurements, therefore, throughout the first year. It is planned to resume electrical conductivity studies early this fall at a time when they can be supplemented by direct optical microscopic observations.

Viscosity Measurements

The device initially used to measure the viscosity of the molten oxide systems at high temperature is the Brookfield Synchro-Electric Viscometer.* The principle of operation of the device is simple. A cylinder or disc or spindle is rotated in the fluid under test through a beryllium-copper spring. The deflection of the spring is read on a dial. The dial reading with the usual disc is multiplied by a simple constant to obtain the resulting viscosity at the particular rotational speed or when special design spindles are used, the device is calibrated through the use of oils of known viscosity. Measurements made at different speeds are used to describe the complete flow properties of the material at hand.

The Brookfield viscometer had never been used before at temperatures as high as those likely to occur in this contract. However, this merely meant that the device must be equipped with a long shaft entering the furnace and with a spindle of suitable high temperature material. Tungsten was selected as the material for both the spindle and shaft because of its known compatibility with all the molten oxide systems investigated to date, and Brookfield Engineering Laboratories then designed the tungsten spindle shown in Fig. 5. This tungsten spindle and the Brookfield viscometer were calibrated using the National Bureau of Standards standard viscosity oil "P" by placing an exact silica replica of the tungsten crucible normally used in the constant temperature bath shown in Fig. 6, filling the silica crucible with oil "P" and running the tungsten spindle in the crucible in such a way as to exactly simulate high temperature operations as shown in Fig. 6. With this constant temperature bath, oil temperatures could be held constant to within ± 0.005 C in the range from -5° to $+107$ C. With this bath, the calibration data obtained for the tungsten spindle is shown in Table II and graphically in Fig. 7.

The viscosity data for N.B.S. standard oil "P" shown as the fourth column of Table II was obtained both by taking the data furnished on the certificate accompanying our shipment of oil "P", plotting it as shown by the solid line of Fig. 8,

*Trade-mark, Brookfield Engineering Laboratories, Inc., Stoughton, Massachusetts

taking the data furnished in the article published by Shartsis and Spinner (Ref. 47) and plotting it as the dotted line of Fig. 8, and extrapolating the solid line of Fig. 8 to give a suitably displaced similarly shaped curve. Experience gained in measuring the viscosity of fused silica (Ref. 48) had shown this procedure to be trustworthy. The completed plot of Fig. 8 is then used to furnish the data tabulated in Table III.

The Brookfield viscometer and tungsten spindle with its elongated shaft were installed on the tungsten resistance furnace as shown in Fig. 9. The spindle is brought out of the tungsten furnace through a high vacuum fitting. Originally the spindle is at rest, the ground glass previously melted in other furnaces is placed in the crucible, the whole system is evacuated, flushed with purified argon by loosening the vacuum fitting and allowing the argon (at a positive pressure of 5 in. of water) to stream out, re-evacuated and refilled with purified argon. The system is heated until the glass is molten as judged by visual examination and the tungsten spindle inserted into the melt and positioned at the proper depth. The temperature of the furnace is adjusted to the desired values and the viscosity of the selected experimental glass is measured at the various temperatures.

Viscosity-temperature curves were measured for sixteen of the experimental molten oxide compositions. The data obtained is given in Table IV and plotted in Figs. 10, 11, 12, 13, and 14. The glass batch numbers used in the compilation can be translated into compositions by the use of Tables I, IA, IB, IC, and ID. It is immediately noticeable that fifteen of the sixteen experimental glasses have much steeper temperature-viscosity curves than the typical commercial "hard" glass plotted for comparison in Fig. 10. One of the experimental glasses, No. 52, shown in Fig. 13 has such a steep temperature-viscosity curve indeed that successful commercial formation of fibers from it is very doubtful. It is probable, however, that glass fibers can be successfully drawn from the other fourteen experimental glasses with steep curves merely by more critically controlled temperatures and the substitution of bushings with specially designed recessed apertures for the conventional bushings. Glass Batch 25 of Fig. 11 whose composition approximates that of beryl is the only experimental composition measured to date with a relatively flat viscosity-temperature relationship and it can probably be made into fibers without any change in existing commercial equipment.

The effect of a progressive change in composition is readily apparent in Fig. 12 where data is plotted for four "invert" glasses. As shown by Table IB additional amounts of titania and of the potassium-calcium-strontium-barium fraction progressively lower the working temperature of the glass.

In Table V, all of the viscosity data obtained has been summarized by listing those temperatures at which a given glass batch has a viscosity of approximately 300 poises. If this data is compared with the data of the next section which lists Young's modulus for the various glass batches by number, it will be apparent that only the high temperature glasses have shown relatively impressively high moduli to date.

In the previous section the procedure for measuring the electrical conductivity of the molten oxides as a continuous function of temperature using a conductivity cell and central "ball" electrode has been described in detail. In this section the method of using the viscometer together with tungsten shaft and spindle to measure viscosity at various temperatures has likewise been described in detail. Since both systems use the same tungsten crucibles with either a rotating tungsten spindle or tungsten ball in the exact center of the crucible, it strongly suggests the possibility that the two measurements can be made simultaneously so as to obtain precise correlation. Numerous methods of making "low" friction electrical contact to the rotating viscometer spindle and shaft were investigated including ball bearings, brushes, and similar methods but all methods investigated were found to be unsatisfactory because of non-reproducible effects on the viscometer readings caused by drag. It does not appear possible, therefore, to make the two measurements simultaneously and we shall continue to carry them out separately.

Elastic Modulus Measurements

Original Equipment for Sonic Determination of Young's Modulus

Apparatus was assembled for measuring Young's modulus on small bulk glass specimens in the form of miniature rectangular beams using sonic techniques. A rectangular or cylindrical beam in flexure vibrates at a resonant frequency determined by the dimensions, density and Young's modulus of the specimen. If shear and inertia effects are considered, the formula for rectangular specimens is

$$E = \frac{(9.65)(10^{-7})ML^3f^2}{a^3b} \left[1 + 7.4 \left(\frac{a}{L} \right)^2 \right] \rightarrow \text{kilograms/cm}^2$$

where M = mass of sample in grams

a = thickness of sample in inches

L = length of sample in inches

b = width of sample in centimeters

f = resonant frequency of sample in cycles/sec

E = Young's modulus for sample in kilograms per square cm.

The equipment used to carry out the measurement is shown in Fig. 15. The specimen is placed on two narrow supports fashioned from sponge rubber, a highly absorbing material. A microphone supplied by a variable frequency oscillator is placed below the center of the specimen. This microphone excites the short column of air between itself and the specimen and this column of air in turn drives the specimen. At a given critical frequency the specimen resonates and this motion is detected by a phonographic pickup cartridge which touches the specimen directly over one of the supports. The signal from the phonographic pickup is then fed through an amplifier to one set of plates of an oscilloscope. The other set of plates of the oscilloscope is supplied from the oscillator output so that at the resonant frequency a Lissajous figure of maximum dimension is seen on the oscilloscope because of the 90° phase shift occurring during detection. At any frequency other than the resonant frequency only a simple horizontal trace forms on the oscilloscope screen so that resonance is readily detectable. The circuitry shown in Fig. 15 when applied to six different specimens of the cordierite based glass yield the data given below.

Dynamic Modulus for Cordierite Based Glasses

| Specimen | Mass gms | Dimensions | | | Young's Modulus | |
|---------------|-------------|------------|--------|---------|---|--|
| | | a (in.) | b (cm) | L (in.) | Kg/cm ² x 10 ⁵ | pounds/in. ² x 10 ⁶ |
| Batch 4 - #1 | 1.2242 | 0.125 | 0.320 | 1.796 | 10.35 | 14.8 |
| Batch 4 - #2 | 1.3698 | 0.1255 | 0.319 | 2.023 | 10.59 | 15.1 |
| Batch 4 - #3 | 1.2508 | 0.126 | 0.320 | 1.850 | 10.55 | 15.0 |
| Batch 14 - #1 | 1.70083 | 0.1273 | 0.324 | 2.406 | 10.52 | 15.0 |
| Batch 14 - #2 | 1.5334 | 0.1275 | 0.324 | 2.173 | 10.55 | 15.0 |
| Batch 14 - #3 | 1.4098 | 0.1277 | 0.324 | 2.025 | 10.74 | 15.0 |

The results obtained are interesting since using the same apparatus values for Corning Glass Works glasses Code 7940 (fused silica) of 10.5×10^6 , Code 7740 (Pyrex) of 9.3×10^6 , and Code 7052 (alumina-silica) of 8.2×10^6 pounds per square inch were obtained. The results obtained are also highly concordant.

Improved Apparatus for the Sonic Determination of Young's Modulus

The equipment used for measurement of Young's modulus and described in the preceding section was entirely satisfactory if glass samples two inches or greater in length were available. But for many glasses without spending undue lengths of

time working out the proper annealing cycle, the longest lengths available are only approximately one inch. To carry out significant measurements on such short samples it was necessary to put together equipment capable of operating at much higher frequencies. This in turn meant purchasing much higher fidelity components.

Equipment selected for improved measurements are shown in Fig. 16. This system shown as a block diagram measures the resonant frequency of glass rods in the region between 1000 and 40,000 Hz. The sample is supported at the nodal points for the fundamental resonance by thin flexible supports that have a resonant frequency below 1000 Hz. A 30 watt driver unit below the center of the sample drives a column of air which in turn excites the sample. The vertical displacement of the end of the bar is detected by the transducer, a high quality semiconductor phonograph cartridge and tone arm adjusted for a tracking force of approximately 0.1 gram. The differential output from the transducer is amplified by a pre-amplifier which also supplies excitation to the transducer. The output of the preamplifier is passed through a high pass R-C filter to remove low frequency noise due to building and support vibrations and is amplified in a guarded differential amplifier. This amplified signal is displayed on a CRO and peak detected to drive the vertical axis of an x-y recorder.

Primary excitation is supplied to the driver unit by a variable frequency audio oscillator through an audio amplifier. A potentiometer mechanically coupled to the frequency control on the oscillator supplies a d-c voltage to the horizontal axis of the x-y recorder proportional to the logarithm of the driving frequency.

With the above system, any spurious resonances due to the driver unit, transducer or supporting structures will appear the same for different samples and can thus be eliminated from the data by the operator. Resonances with amplitudes smaller than those from extraneous sources can be easily resolved by comparative recordings for different sample lengths.

The over-all system has a frequency response from 3000 to 40,000 Hz with an amplitude variation of 3db.

The improved equipment has proven much simpler to use than its immediate predecessor. More than two-thirds of the results shown in Table VI were obtained with this equipment. These results show that research on the cordierite based glass system can consistently yield a glass with a value for Young's modulus in excess of fifteen million psi without any particular annealing cycle. It is, of course, far too early to say whether this value can be further improved.

The degree of consistency obtainable in sonic determinations of Young's modulus with either the older or improved equipment is shown in Table VII. All of the variation present is due to variation in the machined dimensions of the small samples

used. These samples are typically 1.800 inches long, 0.1240 inches wide, and 0.1240 inches high. The commercial lens maker who cuts and grinds these samples for us, of course, has difficulty in holding these dimensions to tolerances better than ± 0.003 inches particularly because these glasses are harder than the usual optical glasses.

The sonic moduli measurements made using glass #1, a cordierite-base glass and similar to batches 4 and 14, were checked using measured deflections versus measured loads in three-point loading apparatus equipped with an unusually sensitive load cell. The comparative results of the two methods are shown in Table VIII. The values obtained by the sonic method are believed to be more nearly correct since this method gives the slope of the initial part of the stress-strain curve and thus corresponds to a value based on microstresses, while the transverse rupture method essentially yields a value for only very large strains and so corresponds to an average value for a stress-strain curve which is not really a straight line when closely examined. Then too, the sonic method applied to commonly available commercial glasses (as mentioned in the first quarterly report) gave values of Young's modulus in complete agreement with the published values. The values obtained by the transverse-deflection method may also be affected by the fact that the glass samples had been stored two months in laboratory atmosphere before these measurements were made, while the sonic moduli values were measured on freshly ground samples. The importance of such aging can only be evaluated through additional experimentation.

Shear Modulus Determined by Velocity of Sound Measurements

The experimental program at this laboratory stresses the rate concept of glass formation from molten oxide solutions of the proper proportions to yield complex three-dimensional ring structures if the glasses from the melt are allowed to devitrify. It is possible, therefore, that the glasses formed from such melts may show anisotropy. Accordingly, UACRL has set up equipment for measuring the shear modulus of the glasses. This determination in conjunction with the sonic determination of Young's modulus will also give values for Poisson's ratio so that any anisotropy in the bulk glass specimen will be apparent.

The equipment assembled for the determination of shear modulus is shown in Fig. 17. As indicated, the circuitry measures the velocity of sound in the sample by driving the transmitting piezoelectric crystal with a short burst of radio-frequency vibrations and measuring the transit time of the pulse in the rod. The transmitted pulse is received by a second piezoelectric crystal acoustically coupled to the far end of the sample.

The pulsed oscillator selected emits a gated burst of high-frequency electrical oscillations in the range of 1.4 Mhz to 60 Mhz (1.4×10^6 to 60×10^6 cycles/sec). This voltage drives the transmitting piezoelectric crystal in the compressional

mode. This crystal is a wafer $1/8$ in. in diameter and $1/64$ in. thick acoustically coupled through oil or cement to the glass specimen and so when it vibrates it causes the glass rod to likewise vibrate in the compressional mode.

The receiving crystal is identical to the transmitting crystal and similarly bonded to the rod so that it is mechanically excited by the compressional waves traveling down the glass bar. The time delay between the transmitted and received pulse is then measured on a dual beam oscilloscope and/or an E-put meter. The velocity of this sound wave and the resulting value for the shear modulus of the specimen are then calculated.

The first measurements on experimental glasses with this new device are scheduled for the early part of the extended contract. The possibility of structure in glass fibers as attested by attendant anisotropy has also been considered by Kroenke (Refs. 16, 17) for those compositions which might give rise to long linear chains such as amphiboles, pyroxenes, diopsides, and spodumenes. He reports that such anisotropy was indeed found in the spodumene based glasses (Ref. 17) but no evidence was found for glasses with values of elastic moduli above 13.2×10^6 psi for these glasses.

Calculation of Young's Modulus of Elasticity from Composition of Simple and Complex Silicate Glasses

In a pioneering paper entitled "Calculation of Young's Modulus of Elasticity from Composition of Simple and Complex Silicate Glasses" (Ref. 40), C. J. Phillips describes a method for calculating Young's modulus of elasticity for some 44 glasses by expressing the content of each oxide in mole percent and multiplying it by a coefficient peculiar to that oxide. Unfortunately, he gives coefficients for only certain oxides likely to be present in glass, namely, SiO_2 , Na_2O , Li_2O , K_2O , B_2O_3 , Al_2O_3 , CaO , MgO , PbO , BaO , ZnO , and BeO . It is hoped that the work of this contract at UACRL can be used to obtain similar values for ZrO_2 , SrO , TiO_2 , Ta_2O_5 , La_2O_3 and other missing oxides. In checking through the paper with our future research in mind, an error was discovered in the coefficient assigned by Phillips to BeO . This error, which has been called to Phillips' attention and with which he agrees, emphasizes the contribution which beryllia is likely to make to high modulus glass research. We submit two examples to show how this type of calculation is carried out and what the correct value of the coefficient for beryllia should be, Tables IXA, IXB.

This value for the beryllia coefficient of 19.0 kilobars/mole % replaces the erroneous value of 24.2 kilobars/mole % which results when glass 73 of the Phillips paper is correctly calculated (Phillips through a juxtaposition of the composition had inadvertently obtained the correct value of the beryllia coefficient). This value of the beryllia coefficient would indicate that the attainment of silica-

base glasses with a modulus greater than 30×10^6 psi is probably impossible. The calculations, however, do not hold for the non-silicate base glasses such as Morey's glasses and the borofluorate glasses of this report nor can they reasonably be expected to hold for Stevels "invert" glasses.

An extension of the Phillips' method of calculation to Loewenstein's glass Z_1^1 (Ref. 51) shows that zirconia has as high a molal Young's modulus factor as beryllia, a fact not noted prior to this report, cf. Table IX.

This value for zirconia is very exciting. Consequently glasses 26, 27, 28, 29, 30, and 31 whose compositions are given in Table ID1 were prepared in this laboratory. But these high zirconia content glasses fail to substantiate the calculated contribution of zirconia to Young's modulus as can be seen from Table VI where the experimentally determined values of Young's modulus for glasses 26, 27, and 29 are listed. This failure, however, may be solely due to the high alkali content of glasses 26 and 27 in contrast to Loewenstein's glass Z_1^1 which has no alkali present. Further research in this area is planned.

Evaluation of Glass Forming Characteristics and Fiberizability

The oxide materials previously melted in the kiln using the procedures described earlier in this report furnish the starting material used in this determination. As a result of their previous heat treatment they are either fully melted glasses, partially melted glasses, or materials that appear like cinders or clinkers or refractories. A sufficient amount of this material is selected to fill a fifteen milliliter platinum crucible. It is then ground or crushed to approximately 10 mesh size and placed in the platinum crucible. The platinum crucible is then placed on the motor-driven platform of the super-kanthal hairpin furnace shown in Fig. 18. The platform is then raised rapidly until the crucible is in the center of the furnace, which is already at the desired temperature. The crucible remains in the furnace chamber for one hour and then is rapidly lowered. Immediately upon its emergence from the furnace the molten contents of the crucible is poured into a small graphite mold which may also be seen in Fig. 18. The glass starts to solidify and as it reaches the proper consistency an attempt is made to pull a fiber from it by hand. The consequences of this set of experiments are found in Table X for the twenty-seven glasses studied to date with this equipment.

CONCLUSIONS

1. Emphasis on research on molten binary and ternary oxide mixtures such as cordierite which form complex three-dimensional molecules appears to form a promising approach to the problem of producing new high modulus glass fibers since bulk glass samples averaging greater than fifteen million psi have resulted in the first year of research from this method of attack. Such research should be continued on a broader basis in the next period of this contract.
2. The study of the variation of electrical conductivity with temperature employed in determining the kinetics of crystallization of molten oxides should be supplemented by concurrent optical microscopic studies to increase its usefulness.
3. Further research on both "invert" glass systems and Morey's non-silica glass systems should be carried out since the first year's research on these systems did not completely answer the question of their usefulness for the production of high modulus glass fibers.
4. Viscosity measurements as a function of temperature, elastic moduli determinations, and fiberizability studies are sufficient to characterize new glass compositions found in this program.

PERSONNEL ACTIVE ON PROGRAM

Personnel active on the program throughout the year have been J. F. Bacon, principal investigator, and Norman J. Chamberlain, senior experimental technician. They were aided repeatedly throughout the year by Louis J. Tempel, Jr. of the UACRL Instrumentation Section. In the second quarter, Charles E. Shulze of the Materials Sciences Section designed, constructed, and operated the equipment used to obtain Young's modulus by the transverse rupture technique. In the third quarter, Herbert G. Aas of the UACRL Instrumentation Section designed the circuitry to be used for shear modulus measurements. In the fourth period John E. Cox of the Materials Sciences Section and his technician, Carl Ravazzoli, carried out the fiberizability studies. Finally, the tantalum furnace and associated fiber pulling equipment mentioned in our future plans were designed and built and loaned to us by John E. Cox and Richard D. Veltri of the Materials Sciences Section. Liaison throughout the program has been carried out by Peter A. Stranges of the UACRL Washington Office.

REFERENCES

1. Machlan, G. R. (Owens-Corning Fiberglas Corp., Newark, Ohio): The Development of Fibrous Glasses Having High Elastic Moduli, November 1955, WADC TR55-290.
2. Waugh, J. F., V. E. J. Chiochetti, H. I. Glaser, and R. Z. Schreffler (Owens-Corning Fiberglas Corp., Newark, Ohio): The Development of Fibrous Glasses Having High Elastic Moduli, Part II, May 1958, WADC TR55-290 - Part II.
3. Frickert, P. J., R. L. Tiede, H. I. Glaser, and A. B. Isham (Owens-Corning Fiberglas Corp., Newark, Ohio): High Modulus, High Temperature Glass Fibers for Reinforced Plastics, November 1960, WADD TR60-24.
4. Machlan, G. R., C. J. Stalego, R. L. Tiede, A. B. Isham, and D. E. Caromente (Owens-Corning Fiberglas Corp., Newark, Ohio): High Modulus, High Temperature Glass Fibers for Reinforced Plastics, Supplement 1, March 1961, WADD TR60-24 - Supplement 1.
5. McMartin, R. M., R. L. Tiede, F. M. Veazie (Owens-Corning Fiberglas Corp., Newark, Ohio): High Strength-High Modulus Glass Fibers, March 1965, AFML-TR-65-90 - Part I.
6. Lambertson, W. A., D. B. Aiken, and E. H. Girard (The Carborundum Co., Research and Development Division): Continuous Filament Ceramic Fibers, June 1960, WADD TR60-244.
7. Girard, E. H. (The Carborundum Co., Research and Development Division): Continuous Filament Ceramic Fibers, Part II, February 1961, WADD TR60-244.
8. Drummond, W. W., and B. A. Cash (Bjorksten Research Labs., Inc., Madison Wisconsin): Development of Textile Type Vitreous Silica Yarns, Final Report, March 1960, WADC 59-699.
9. Nagler, R. T. (Bjorksten Research Labs., Inc., Madison, Wisconsin): High Viscosity Refractory Fibers, Quarterly Report #1, 1 July - 30 September 1958, Contract NOrd-18492, AD 209137.
10. Drummond, W. W. (Bjorksten Research Labs., Inc., Madison, Wisconsin): High Viscosity Refractory Fibers, Quarterly Report #2, 1 October - 31 December 1958, NOrd-18492, AD 210948.

11. Dunn, S. A., and W. P. Roth (Bjorksten Research Labs., Inc., Madison, Wisconsin): High Viscosity Refractory Fibers, Quarterly Report #3, 20 April - 20 July 1960, NOrd-19100, AD 242218.
12. Dunn, S. A., and W. P. Roth (Bjorksten Research Labs., Inc., Madison, Wisconsin): High Viscosity Refractory Fibers, Quarterly Report #5, 30 October - 31 January 1961, NOrd-19100.
13. Rowe, E., D. Silvey, and G. Thomas (B. F. Goodrich Research Center, Brecksville, Ohio): New High-Strength Glasses. Paper presented at Sect. 4-C, 18th Annual Conference, Tech. & Management, Reinforced Plastic Division, Sect. 4-C - Pages 1-8, February 5,6,7, 1963. Chicago, Illinois, The Society of the Plastics Industry, Inc.
14. Kroenke, W. J., E. H. Rowe, and G. L. Thomas (B. F. Goodrich Research Center, Brecksville, Ohio): Structured Glasses Patterned After Asbestos, Part I, April 30, 1963, RFD-TDR-63-4043 - Part I, Contract AF33(657)8905.
15. Kroenke, W. J. (B. F. Goodrich Research Center, Brecksville, Ohio): Linear Structured Glass Fibers, Quarterly Progress Report (9-1-64 to 11-30-64), AF33(657)8905.
16. Kroenke, W. J. (B. F. Goodrich Research Center, Brecksville, Ohio): Flexible Glass Fibers, March 1964, TDR-ML-TDR-64-119, Contract AF33(657)8905, Project 7320 - Task No. 732001.
17. Kroenke, W. J. (B. F. Goodrich Research Center, Brecksville, Ohio): Anisotropic Glass Fibers and Property-Composition Relationships. AFML-TR-65-189, 1965, Contract AF33(657)8905, Project 7320, Task 732001.
18. Otto, W. H. (Narmco Research & Development Division, San Diego, California 92123): Silica Fiber Forming and Core Sheath Composite Fiber Development, Final Summary Technical Report, 3 January 1964, Navy, BuWeps, N600(19)59607.
19. Otto, W. H. (Narmco Research & Development Division, Whittaker Corporation, San Diego, California 92123): Silica Fiber/Core-Sheath Fiber, Quarterly Progress Report #1, 30 May 1964, BuWeps, N600(19)61810.
20. Otto, W. H. (Narmco Research and Development Division, Whittaker Corporation, San Diego, California 92123): Silica Fiber/Core-Sheath Fiber, Quarterly Progress Report #2, 31 August 1964, BuWeps N600(19)61810.

21. Otto, W. H. (Narmco Research and Development Division, Whittaker Corp., San Diego, California 92123): Silica Fiber/Core-Sheath Fiber/High-Temperature Oxide Fibers, Quarterly Progress Report #4, 10 February 1965, BuWeps, N600(19)61810.
22. Otto, W. H., D. Plaskon, and D. Bradford (Narmco Research & Development Division Whittaker Corp., San Diego, California 92123): Silica Fiber/Core-Sheath Fiber, Final Technical Report, Navy, BuWeps, Contract N600(19)61810, Issued 15 June 1965 and covering 1 February 1964 - 1 June 1965.
23. Schmitz, G. K., and A. G. Metcalfe (Solar, Subsidiary of International Harvester Co., San Diego 12, California 92112): Exploration and Evaluation of New Glasses in Fiber Form. Final Report, 12 April 1963 - NRL Project 62, R05 19A, RDR 1266-7.
24. Schmitz, G. K. (Solar, Subsidiary of International Harvester Co., San Diego 12, California 92112): Exploration and Evaluation of New Glasses in Fiber Form, (2nd contract year), Bimonthly Progress Report #2, 24 June 1963, RDR 1343-2.
25. Schmitz, G. K., and A. G. Metcalfe (Solar, Subsidiary of International Harvester Co., San Diego 12, California 92112): Exploration and Evaluation of New Glasses in Fiber Form. Bimonthly Progress Report #6 (3rd contract year), 1 November through 31 December 1964, NRL Project 62, R05 19A, Contract NONR 3654(00) (X) A2, 15 January 1965.
26. Davies, L. G., and J. C. Withers (General Technologies Corp., Materials Division, Alexandria, Virginia): A Study of High Modulus, High Strength Filament Materials by Deposition Techniques, 1st Bimonthly Report, January 15, 1964, Contract NOW 64-0176-E N64 14676, Unclassified, Code 3.
27. through 34. Capps, W., D. H. Blackburn, M. H. Black, H. F. Shermer, and A. A. Edwards: The Development of Glass Fibers Having High Young's Moduli of Elasticity. Nat. Bur. of Standards Reports 3978, 4176, 4318, 4417, 4572, 4699, 4850, 5188. Bur. Ord., U. S. Navy Contract IPR NOrd 03046 (December 1954 - April 1, 1957), NBS Project 0902-20-4464.
35. Lasday, A. H. (Houze Glass Corp.): Development of High Modulus Fibers from Heat Resistant Materials, October 1958, WADC TR58-285, ASTIA Doc. #202500, Contract AF33(616)-5263, Project 7340.
36. Brossy, J. F., and J. D. Provance (Houze Glass Corp.): Development of High Modulus Fibers from Heat Resistant Materials, March 1960, WADC TR58-285, Part II, ASTIA Doc. #236991, Contract AF33(616)-5263, Project 7340.

37. Lewis, A., and D. L. Robbins (Glass Technology Section, Von Karman Research Center, Aerojet-General Corporation, Azusa, California): High-Strength, High-Modulus Glass Filaments, April 1965, AFML-TR-65-132 - Part I.
38. Gates, L. E., and W. E. Lent: Studies on Refractory Fiber Research, 30 October 1960 - Contract DA-04-495-ORD-1723 between Army Ballistic Missile Agency, U. S. Army Ordnance Corps and Components Division, Hughes Aircraft Company, Culver City, California.
39. Gates, L. E., and W. E. Lent: Development of Refractory Fabrics, Final Summary Report, 8 April 1963 covering period 1 October 1960 to 2 December 1962, Contract NAS 8-50 between NASA, George C. Marshall Space Flight Center and Components & Materials Laboratory, Hughes Aircraft Company, Culver City, California.
40. Phillips, C. J.: Calculation of Young's Modulus of Elasticity from Composition of Simple and Complex Silicate Glasses. Glass Technology, Vol. 5, No. 6, December 1964, pg. 216-223.
41. Kuan-Han Sun: U. S. Patent 2,456,033, issued December 14, 1948.
42. Weissenberg, Gustav and Otto Ungemach: U. S. Patent 2,764,492, issued September 25, 1956.
43. Morey, George W.: U. S. Patent 2,150,694, issued March 14, 1939.
44. DePaoli, Paul F.: U. S. Patent 2,787,554, issued April 2, 1957.
45. Weyl, Woldemar A. and Evelyn C. Marbo: The Constitution of Glasses, Vol. II - Constitution and Properties of Some Representative Glasses, pg. 820, Interscience Publ., New York, 1964.
46. Burke, J. E.: Progress in Ceramic Science, Vol. I, Chapter 5, R. W. Douglas, The Properties and Structure of Glasses, pg. 203-204, Pergamon Press, New York, 1961.
47. Sharsis, Leo and Sam Spinner: Viscosity and Density of Molten Optical Glasses. Journ. Res. N. B. S., Vol. 46, No. 3, March 1951, R. P. 2190, pg. 176-194.
48. Bacon, James F., Alex A. Hasapis and James W. Wholley, Jr.: Viscosity and Density of Molten Silica and High Silica Content Glasses. Physics and Chemistry of Glasses, Vol. 1, No. 3, June 1960, pg. 90-98.

49. McMarlin, Robert M., Owens-Corning, Telephone Conversation on January 20, 1966 with J. F. Bacon, UACRL.
50. Tiede, Ralph L: U. S. Patent 3,127,277, issued March 31, 1964, Example 4.
51. Loewenstein, K. L.: Studies in the Composition and Structure of Glasses Possessing High Young's Moduli. Part I. The Composition of High Young's Modulus Glass and the Function of Individual Ions in the Glass Structure. Physics and Chemistry of Glasses, Vol. 2, No. 3, June 1961, pg. 69-82.

TABLE I

Number of Table in Which A Given Batch
Composition is Found

| <u>Batch</u> | <u>Table</u> | <u>Batch</u> | <u>Table</u> | <u>Batch</u> | <u>Table</u> |
|--------------|--------------|--------------|--------------|--------------|--------------|
| 1 | IA | 28 | ID1 | 55, 55A, 55B | IB |
| 2 | IC | 29 | ID1 | 56 | ID6 |
| 3 | ID6 | 30 | ID1 | 57 | ID2 |
| 4 | IA | 31 | ID1 | 58 | ID2 |
| 5 | ID6 | 32 | ID4 | 59 | IC |
| 6 | IA | 33 | ID4 | 60 | IC |
| 7 | IA | 34 | ID4 | 61 | IC |
| 8 | IC | 35 | ID4 | 62 | IA |
| 9 | IC | 36 | IA | 63 | IA |
| 10 | IC | 37 | IA | 64 | IA |
| 11 | IA | 38 | IA | 65 | IA |
| 12 | ID6 | 39 | IA | 66 | IA |
| 13 | IA | 40 | IA | 67 | IA |
| 14 | IA | 41 | IB | 68 | IA |
| 15 | IA | 42 | IB | 69 | IA |
| 16 | IA | 43 | IB | 70 | IA |
| 17 | IA | 44, 44A | IB | 71 | IA |
| 18 | IA | 45 | IB | 72 | IA |
| 19 | IA | 46, 46B | IB | 73 | IA |
| 20 | IC | 47, 47B | IB | 74 | IA |
| 21 | IA | 48, 48B | IB | 75 | ID3 |
| 22 | IC | 49, 49B | IB | 76 | ID3 |
| 23 | ID2 | 50, 50B | IB | 77 | ID3 |
| 24 | IA | 51, 51B | IB | 78 | ID2 |
| 25 | ID6 | 52, 52B | IB | 79 | ID6 |
| 26 | ID1 | 53, 53B | IB | 80 | ID6 |
| 27 | ID1 | 54, 54A, 54B | IB | 81 | ID6 |
| | | | | 82 | ID5 |
| | | | | 83 | ID5 |

TABLE IA

Preparation of Cordierite-Type Glasses with Nucleating
and Anti-Nucleating Additions

| <u>Ingredient</u> | <u>Batch No. (amounts of components in grams)</u> | | | | | | | |
|-----------------------------|---|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| | <u>1*</u> | <u>36</u> | <u>37</u> | <u>38</u> | <u>39</u> | <u>40</u> | | |
| Silica | 198.0 | 149.0 | 149.0 | 149.0 | 149.0 | 149.0 | | |
| Alumina | 120.0 | 90.0 | 90.0 | 90.0 | 90.0 | 90.0 | | |
| Magnesium Carbonate (basic) | 180.0 | 135.0 | 135.0 | 135.0 | 135.0 | 135.0 | | |
| Beryllium Carbonate | --- | 135.0 | --- | --- | --- | --- | | |
| Zirconium Carbonate | --- | --- | 75.0 | --- | --- | --- | | |
| Lithium Carbonate | --- | --- | --- | 123.5 | --- | --- | | |
| Zinc Oxide | --- | --- | --- | --- | 37.5 | --- | | |
| Cerium Oxalate | --- | --- | --- | --- | --- | 135.0 | | |
| | <u>62</u> | <u>63</u> | <u>64</u> | <u>65</u> | <u>66</u> | <u>67</u> | <u>68</u> | <u>69</u> |
| Silica | 258.0 | 258.0 | 258.0 | 258.0 | 258.0 | 258.0 | 258.0 | 283.0 |
| Alumina | 125.0 | 125.0 | 125.0 | 125.0 | 125.0 | 125.0 | 150.0 | 125.0 |
| Magnesium Carbonate (basic) | 192.0 | 192.0 | 192.0 | 192.0 | 192.0 | 192.0 | 192.0 | 192.0 |
| Cerium Oxalate | 54.0 | --- | --- | --- | --- | --- | --- | --- |
| Lanthanum Oxalate | --- | 54.0 | --- | --- | --- | --- | --- | --- |
| Yttrium Oxalate | --- | --- | 67.0 | --- | --- | --- | --- | --- |
| Samarium Oxalate | --- | --- | --- | 53.5 | --- | --- | --- | --- |
| Zirconium Carbonate | --- | --- | --- | --- | 28.0 | --- | --- | --- |
| Tantalum Oxide | --- | --- | --- | --- | --- | 25.0 | --- | --- |
| | <u>70</u> | <u>71</u> | <u>72</u> | <u>73</u> | <u>74</u> | | | |
| Silica | 258.0 | 250.0 | 250.0 | 250.0 | 258.0 | | | |
| Alumina | 100.0 | 125.0 | 112.5 | 62.5 | 75.0 | | | |
| Magnesium Carbonate (basic) | 192.0 | 261.5 | 157.0 | 157.0 | 192.0 | | | |
| Yttrium Oxalate | 134.0 | --- | --- | 134.0 | 191.0 | | | |
| Cerium Oxalate | --- | --- | 135.0 | 135.0 | --- | | | |

* Also batches 4, 6, 7, 11, 13, 14, 15, 16, 17, 18, 19, 21, 24

TABLE IB

Preparation of "Invert" Glasses

| <u>Ingredient</u> | <u>Batch No. (amounts of components in grams)</u> | | | | | | | |
|---------------------|---|-----------|------------|-----------|------------|-----------|------------|-----------|
| | <u>41</u> | <u>42</u> | <u>43</u> | <u>44</u> | <u>44A</u> | <u>45</u> | <u>46</u> | |
| Silica | 176.0 | 176.0 | 176.0 | 176.0 | 176.0 | 200.0 | 325.0 | |
| Lead Carbonate | 57.6 | 57.6 | 57.6 | --- | --- | --- | --- | |
| Titanium Nitrate | --- | 92.0 | 18.4 | --- | --- | --- | --- | |
| Rutile | --- | --- | --- | 48.0 | 24.0 | --- | 35.0 | |
| Titanium Dioxide | --- | --- | --- | --- | 24.0 | --- | --- | |
| Zirconium Carbonate | --- | --- | --- | --- | --- | --- | --- | |
| Potassium Carbonate | 75.4 | 34.99 | 75.5 | 75.5 | 75.5 | 85.75 | 60.0 | |
| Calcium Carbonate | 78.5 | 42.82 | 78.5 | 78.5 | 78.5 | 89.20 | 62.4 | |
| Strontium Carbonate | 62.7 | 34.2 | 62.7 | 62.7 | 62.7 | 71.25 | 49.8 | |
| Barium Carbonate | 57.2 | 31.2 | 57.2 | 57.2 | 57.2 | 65.0 | 45.5 | |
| | <u>46B</u> | <u>47</u> | <u>47B</u> | <u>48</u> | <u>48B</u> | <u>49</u> | <u>49B</u> | <u>50</u> |
| Silica | 267.0 | 300.0 | 241.75 | 250.0 | 190.75 | 240.0 | 183.5 | 225.0 |
| Lead Carbonate | --- | --- | --- | --- | --- | --- | --- | --- |
| Titanium Nitrate | --- | --- | --- | --- | --- | --- | --- | --- |
| Rutile | --- | 50.0 | --- | 50.0 | --- | 65.0 | --- | --- |
| Titanium Dioxide | 38.15 | --- | 53.5 | --- | 50.65 | --- | 65.25 | 55.0 |
| Zirconium Carbonate | --- | --- | --- | --- | --- | --- | --- | --- |
| Potassium Carbonate | 77.2 | 64.3 | 80.2 | 85.8 | 83.4 | 83.5 | 99.1 | 94.2 |
| Calcium Carbonate | 47.75 | 66.9 | 50.3 | 88.8 | 63.3 | 87.0 | 61.3 | 98.2 |
| Strontium Carbonate | 70.50 | 53.4 | 74.2 | 71.25 | 93.6 | 69.4 | 90.5 | 78.4 |
| Barium Carbonate | 95.25 | 48.5 | 100.3 | 65.0 | 126.3 | 63.3 | 124.2 | 71.5 |
| | <u>50B</u> | <u>51</u> | <u>51B</u> | <u>52</u> | <u>52B</u> | <u>53</u> | <u>53B</u> | |
| Silica | 168.0 | 190.0 | 139.75 | 190.0 | 130.0 | 175.0 | 125.65 | |
| Rutile | --- | 103.3 | --- | 103.3 | --- | 65.0 | --- | |
| Titanium Dioxide | 54.55 | --- | 103.30 | --- | 76.75 | --- | 62.0 | |
| Potassium Carbonate | 110.3 | 88.5 | 102.5 | 88.5 | 116.3 | 111.4 | 125.3 | |
| Calcium Carbonate | 68.2 | 92.2 | 63.3 | 92.2 | 71.3 | 115.8 | 77.75 | |
| Strontium Carbonate | 100.7 | 73.6 | 93.7 | 73.6 | 106.3 | 92.6 | 114.6 | |
| Barium Carbonate | 136.2 | 67.2 | 126.3 | 67.2 | 143.5 | 84.5 | 149.0 | |

TABLE IB (Contd.)

| <u>Ingredient</u> | Batch No. (amounts of components in grams) | | | | | |
|---------------------|--|------------|------------|-----------|------------|------------|
| | <u>54</u> | <u>54A</u> | <u>54B</u> | <u>55</u> | <u>55A</u> | <u>55B</u> |
| Silica | 170.0 | 175.0 | 123.2 | 170.0 | 175.0 | 110.8 |
| Rutile | 110.0 | --- | --- | --- | --- | --- |
| Titanium Dioxide | --- | 105.0 | 105.9 | --- | --- | --- |
| Zirconia | --- | --- | --- | 110.0 | 117.81 | 165.0 |
| Potassium Carbonate | 94.3 | 94.3 | 107.2 | 94.3 | 94.3 | 96.4 |
| Calcium Carbonate | 98.2 | 98.2 | 66.6 | 98.2 | 98.2 | 59.4 |
| Strontium Carbonate | 78.4 | 78.4 | 97.7 | 78.4 | 78.4 | 87.8 |
| Barium Carbonate | 71.5 | 71.5 | 132.2 | 71.5 | 71.5 | 118.5 |

TABLE IC

Non-Silica Containing Glasses of Morey-DePaolis Type

| <u>Ingredient</u> | Batch No. (amounts of components in grams) | | | | | |
|---------------------|--|-----------|-----------|-----------|-----------|-----------|
| | <u>2</u> | <u>8</u> | <u>9</u> | <u>10</u> | <u>20</u> | <u>22</u> |
| Zirconia | 75.0 | --- | --- | 20.0 | --- | --- |
| Titanium Dioxide | 200.0 | 50.0 | --- | 20.0 | --- | 50.0 |
| Tantalum Oxide | 225.0 | 50.0 | 50.0 | 30.0 | 146.0 | 75.0 |
| Silica | --- | --- | 50.0 | 30.0 | --- | 75.0 |
| Zirconium Carbonate | --- | --- | --- | --- | --- | 61.5 |
| Lanthanum Oxalate | --- | --- | --- | --- | 427.0 | --- |
| Thoria | --- | --- | --- | --- | 83.5 | --- |
| Fused Boric Acid | --- | --- | --- | --- | 83.0 | --- |
| | | <u>59</u> | <u>60</u> | <u>61</u> | | |
| Lanthanum Oxalate | | 407.0 | 434.0 | 293.0 | | |
| Tantalum Oxide | | 146.0 | 55.0 | 80.0 | | |
| Thorium Dioxide | | 83.5 | 30.0 | 80.0 | | |
| Boric Acid | | 147.5 | 195.5 | 212.0 | | |
| Strontium Carbonate | | --- | 25.0 | --- | | |
| Barium Carbonate | | --- | 10.0 | --- | | |
| Tungsten Oxide | | --- | 11.7 | 10.0 | | |
| Silica | | --- | 12.5 | --- | | |
| Alumina | | --- | 17.5 | 15.0 | | |
| Titanium Dioxide | | --- | 15.0 | --- | | |
| Zirconium Dioxide | | --- | 50.0 | 60.0 | | |
| Lithium Carbonate | | --- | 2.5 | --- | | |

TABLE ID

Preparation of Various Glasses Including Those with High-Zirconia
Content, Beryl or Benitoite or Fluoborate Base,
Two-Component Systems and Miscellaneous

1. High Zirconia Content Glasses

| <u>Ingredient</u> | Batch No. (amounts of components in grams) | | | |
|---------------------|--|--------------|-----------|-----------|
| | <u>26,30</u> | <u>27,31</u> | <u>28</u> | <u>29</u> |
| Silica | 360.5 | 310.0 | 138.0 | 177.5 |
| Sodium Carbonate | 144.4 | 119.7 | --- | --- |
| Alumina | 4.3 | 4.0 | 142.0 | 145.5 |
| Rutile | 1.00 | --- | --- | --- |
| Calcium Carbonate | --- | 4.36 | 68.7 | 47.3 |
| Potassium Carbonate | --- | 14.6 | --- | --- |
| Anhydri Boric Oxide | --- | --- | 51.0 | 47.5 |
| Beryllium Carbonate | --- | --- | --- | 75.90 |
| Cerium Oxide | --- | --- | 72.0 | --- |
| Zirconium Carbonate | 58.00 | 117.8 | 75.2 | 77.4 |

2. Two Oxide Systems

| <u>Ingredient</u> | Batch No. (amounts of components in grams) | | | |
|---------------------|--|-----------|-----------|-----------|
| | <u>23</u> | <u>57</u> | <u>58</u> | <u>78</u> |
| Alumina | 100.0 | 276.5 | 491.5 | --- |
| Zirconium Carbonate | 123.0 | 250.5 | --- | --- |
| Calcium Carbonate | --- | --- | 15.15 | --- |
| Silica | --- | --- | --- | 460.0 |
| Titanium Oxalate | --- | --- | --- | 80.0 |

TABLE ID (Contd.)

3. Three Oxide System

| <u>Ingredient</u> | Batch No. (amounts of components in grams) | | |
|-------------------|--|-----------|-----------|
| | <u>75</u> | <u>76</u> | <u>77</u> |
| Silica | 310.0 | 310.0 | 310.0 |
| Sodium Carbonate | 153.9 | 111.11 | 68.4 |
| Calcium Carbonate | 178.4 | 223.0 | 267.6 |

4. Fluoborate and Lanthanum Borate Glasses

| <u>Ingredient</u> | Batch No. (amounts of components in grams) | | | |
|--------------------------|--|-----------|-----------|-----------|
| | <u>32</u> | <u>33</u> | <u>34</u> | <u>35</u> |
| Calcium Fluoride | 240.0 | 30.0 | 180.0 | 20.0 |
| Boric Acid (H_3BO_3) | --- | --- | 346.5 | 142.0 |
| Boric Anhydride | 260.0 | 120.0 | --- | --- |
| Lanthanum Oxalate | --- | 409.0 | --- | 217.0 |
| Zirconia | --- | 50.0 | --- | 25.0 |

5. Glasses Prepared for Comparative Measurements from Published Data

| <u>Ingredient</u> | Batch No. (amounts of components in grams) | |
|-----------------------------|--|-----------|
| | <u>82</u> | <u>83</u> |
| Silica | 235.0 | 255.0 |
| Alumina | 180.0 | --- |
| Zirconium Carbonate | 22.44 | 11.22 |
| Magnesium Carbonate (basic) | 109.83 | 104.14 |
| Sodium Carbonate | 4.28 | --- |
| Calcium Carbonate | --- | 115.96 |
| Beryllium Carbonate | --- | 121.0 |
| Titania (not Rutile) | --- | 40.0 |
| Lithium Carbonate | --- | 37.1 |
| Cerium Oxalate | --- | 32.25 |

TABLE ID (Contd.)

6. Beryl and Benitoite Based Systems, ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ and $\text{BaTiSi}_3\text{O}_9$)

| <u>Ingredient</u> | Batch No. (amounts of components in grams) | |
|-----------------------------|--|-----------------|
| | <u>25</u> | <u>3, 5, 12</u> |
| Silica | 250.0 | 88.5 |
| Alumina | 175.0 | --- |
| Magnesium Carbonate (basic) | 80.0 | --- |
| Beryllium Carbonate | 80.0 | --- |
| Barium Carbonate | --- | 355.0 |
| Titanium Dioxide | --- | 141.5 |

7. Miscellaneous Oxide Systems

| <u>Ingredient</u> | Batch No. (amounts of components in grams) | | | |
|-----------------------------|--|-----------|-----------|-----------|
| | <u>56</u> | <u>79</u> | <u>80</u> | <u>81</u> |
| Silica | 382.5 | 155.0 | 20.4 | 160.0 |
| Lithium Carbonate | 185.5 | --- | --- | --- |
| Phosphorus Pentoxide | 5.0 | --- | --- | --- |
| Zinc Carbonate | 57.75 | --- | --- | --- |
| Boric Acid | --- | 106.5 | --- | --- |
| Calcium Carbonate | --- | 428.0 | 261.6 | 321.0 |
| Yttrium Oxalate | --- | 120.5 | 315.6 | 201.0 |
| Magnesium Carbonate (basic) | --- | --- | 31.4 | 10.45 |
| Sodium Carbonate | --- | --- | --- | 17.1 |
| Ferric Oxide | --- | --- | --- | 35.0 |

TABLE II

Calibration of Large Tungsten Spindle in N.B.S. Standard Oil "P"

| <u>Viscometer Speed(rpm)</u> | <u>Reading (arb. div.)</u> | <u>Temp. (°C)</u> | <u>Viscosity Oil P (poises)</u> |
|----------------------------------|--------------------------------|-----------------------|-------------------------------------|
| 20.0 | 74.0 | 51.0 | 80 |
| 20.0 | 79.5 | 47.5 | 111 |
| 20.0 | 95.7 | 44.0 | 145 |
| 10.0 | 37.2 | 51.0 | 80 |
| 10.0 | 39.8 | 47.5 | 111 |
| 10.0 | 48.1 | 44.0 | 145 |
| 10.0 | 73.0 | 41.0 | 175 |
| 5.0 | 18.3 | 51.0 | 80 |
| 5.0 | 19.6 | 47.5 | 111 |
| 5.0 | 24.0 | 44.0 | 145 |
| 5.0 | 36.5 | 41.0 | 175 |
| 5.0 | 52.0 | 37.9 | 214 |
| 5.0 | 60.5 | 35.0 | 275 |
| 5.0 | 66.0 | 32.0 | 362 |
| 5.0 | 81.1 | 29.0 | 450 |
| 5.0 | 82.7 | 28.0 | 510 |
| 2.5 | 9.4 | 51.0 | 80 |
| 2.5 | 9.75 | 47.5 | 111 |
| 2.5 | 12.1 | 44.1 | 145 |
| 2.5 | 18.4 | 41.0 | 175 |
| 2.5 | 25.5 | 38.0 | 214 |
| 2.5 | 30.4 | 35.0 | 275 |
| 2.5 | 36.5 | 32.0 | 362 |
| 2.5 | 41.4 | 29.0 | 450 |
| 2.5 | 41.0 | 28.0 | 510 |
| 2.5 | 48.7 | 27.0 | 555 |
| 2.5 | 65.2 | 24.0 | 780 |
| 2.5 | 81.8 | 21.0 | 970 |
| 2.5 | 83.6 | 18.0 | 1290 |

TABLE II (Contd.)

| <u>Viscometer Speed(rpm)</u> | <u>Reading (arb. div.)</u> | <u>Temp. (°C)</u> | <u>Viscosity Oil P (poises)</u> |
|----------------------------------|--------------------------------|-----------------------|-------------------------------------|
| 1.0 | 4.05 | 51.0 | 80 |
| 1.0 | 4.45 | 47.5 | 111 |
| 1.0 | 4.9 | 44.0 | 145 |
| 1.0 | 7.5 | 41.0 | 175 |
| 1.0 | 10.1 | 37.9 | 214 |
| 1.0 | 12.4 | 35.0 | 275 |
| 1.0 | 14.2 | 32.0 | 362 |
| 1.0 | 16.4 | 29.0 | 450 |
| 1.0 | 16.5 | 28.0 | 510 |
| 1.0 | 19.5 | 27.0 | 555 |
| 1.0 | 26.1 | 24.0 | 780 |
| 1.0 | 32.5 | 21.0 | 970 |
| 1.0 | 31.6 | 18.0 | 1290 |
| 1.0 | 66.3 | 14.8 | 1790 |
| 1.0 | 88.3 | 12.0 | 2380 |
| 0.5 | 2.85 | 44.1 | 145 |
| 0.5 | 4.2 | 41.0 | 175 |
| 0.5 | 5.6 | 37.9 | 214 |
| 0.5 | 6.6 | 35.0 | 275 |
| 0.5 | 7.7 | 32.0 | 362 |
| 0.5 | 8.8 | 29.0 | 450 |
| 0.5 | 8.8 | 28.0 | 510 |
| 0.5 | 10.0 | 27.0 | 555 |
| 0.5 | 13.5 | 24.0 | 780 |
| 0.5 | 16.8 | 21.0 | 970 |
| 0.5 | 16.8 | 18.0 | 1290 |
| 0.5 | 35.5 | 14.9 | 1790 |
| 0.5 | 46.75 | 12.0 | 2380 |
| 0.5 | 51.2 | 9.0 | off graph used |
| 0.5 | 57.5 | 5.85 | off graph used |

TABLE III

Extrapolated and Certificate Values of Viscosity for
N.B.S. Viscosity Standard Oil "P"

| <u>Temperature °C</u> | <u>Viscosity (poises)</u> | <u>Temperature °C</u> | <u>Viscosity (poises)</u> |
|-----------------------|---------------------------|-----------------------|---------------------------|
| 30.0 | 417.8 certif. | 33.36 | 329 (Ref. 8) |
| 40.0 | 183.3 certif. | 29.50 | 448 (Ref. 8) |
| 50.0 | 86.6 certif. | 26.98 | 569 (Ref. 8) |
| | | 11.98 | 2,439 (Ref. 8) |
| | | 19.10 | 1,193 (Ref. 8) |
| | | 11.81 | 2,499 (Ref. 8) |

TABLE IV

Experimental Determination of Viscosity Individual Runs

| Glass Batch No. 1 | | Glass Batch No. 25 | | Glass Batch No. 30 | |
|-------------------|-----------------------|--------------------|-----------------------|--------------------|-----------------------|
| Temp. °C | Viscosity (poises) | Temp. °C | Viscosity (poises) | Temp. °C | Viscosity (poises) |
| 1281 | 2150 | 1478 | 200 | 1247 | 1310 |
| 1305 | 335 | 1488 | 140 | 1267 | 954 |
| 1313 | 184 | 1498 | 115 | 1292 | 765 |
| 1333 | 160 | 1509 | 80 | 1305 | 557 |
| 1348 | 87 | | | 1327 | 365 |
| | | | | 1342 | 281 |
| | | | | 1377 | 193 |
| | | | | 1392 | 186 |

| Glass Batch No. 24 | | Glass Batch No. 31 | | Glass Batch No. 41 | |
|--------------------|-----------------------|--------------------|-----------------------|--------------------|-----------------------|
| Temp. °C | Viscosity (poises) | Temp. °C | Viscosity (poises) | Temp. °C | Viscosity (poises) |
| 1350 | 1600 | 1358 | 1043 | 905 | 880 |
| 1365 | 1285 | 1378 | 947 | 925 | 320 |
| 1385 | 1050 | 1405 | 748 | 935 | 210 |
| 1407 | 685 | 1420 | 475 | 959 | 160 |
| 1420 | 450 | 1445 | 373 | 969 | 160 |
| 1450 | 275 | 1455 | 270 | | |
| 1485 | 200 | 1483 | 213 | | |
| 1500 | 175 | 1492 | 175 | | |
| 1520 | 150 | 1508 | 170 | | |
| 1540 | 130 | 1532 | 147 | | |
| 1570 | 95 | 1558 | 57 | | |
| 1590 | 80 | | | | |

TABLE IV (Contd.)

| Glass Batch No. 43 | |
|--------------------|-----------------------|
| Temp. °C | Viscosity (poises) |
| 983 | 2500 |
| 1005 | 1425 |
| 1030 | 965 |
| 1060 | 300 |
| 1080 | 190 |
| 1103 | 165 |
| 1115 | 135 |

| Glass Batch No. 45 | |
|--------------------|-----------------------|
| Temp. °C | Viscosity (poises) |
| 1077 | 1750 |
| 1112 | 600 |
| 1145 | 300 |
| 1160 | 175 |

| Glass Batch No. 46 | |
|--------------------|-----------------------|
| Temp. °C | Viscosity (poises) |
| 1143 | 2100 |
| 1157 | 1690 |
| 1177 | 1335 |
| 1209 | 905 |
| 1227 | 570 |
| 1237 | 450 |
| 1254 | 275 |
| 1266 | 235 |
| 1278 | 190 |

| Glass Batch No. 48 | |
|--------------------|-----------------------|
| Temp. °C | Viscosity (poises) |
| 1038 | 1590 |
| 1062 | 920 |
| 1090 | 535 |
| 1110 | 280 |
| 1137 | 210 |
| 1140 | 180 |

| Glass Batch No. 49 | |
|--------------------|-----------------------|
| Temp. °C | Viscosity (poises) |
| 1011 | 2500 |
| 1025 | 1630 |
| 1042 | 1080 |
| 1050 | 930 |
| 1057 | 725 |
| 1087 | 345 |
| 1110 | 200 |
| 1128 | 170 |

| Glass Batch No. 50 | |
|--------------------|-----------------------|
| Temp. °C | Viscosity (poises) |
| 1009 | 3000 |
| 1040 | 1000 |
| 1067 | 320 |
| 1078 | 205 |

TABLE IV (Contd.)

Glass Batch No. 52

| Temp. °C | Viscosity (poises) |
|-------------|-----------------------|
|-------------|-----------------------|

| | |
|------|------|
| 1034 | 4500 |
| 1039 | 2700 |
| 1050 | 1760 |
| 1072 | 910 |
| 1083 | 180 |

Glass Batch No. 63-2

| Temp. °C | Viscosity (poises) |
|-------------|-----------------------|
|-------------|-----------------------|

| | |
|------|------|
| 1157 | 2600 |
| 1170 | 2060 |
| 1193 | 1500 |
| 1223 | 900 |
| 1231 | 725 |
| 1248 | 520 |
| 1268 | 330 |
| 1287 | 235 |
| 1310 | 200 |

Glass Batch No. 64

| Temp. °C | Viscosity (poises) |
|-------------|-----------------------|
|-------------|-----------------------|

| | |
|------|------|
| 1207 | 2300 |
| 1228 | 1630 |
| 1250 | 1030 |
| 1265 | 825 |
| 1276 | 615 |
| 1299 | 365 |
| 1326 | 210 |
| 1340 | 190 |

Glass Batch No. 65

| Temp. °C | Viscosity (poises) |
|-------------|-----------------------|
|-------------|-----------------------|

| | |
|------|------|
| 1173 | 2900 |
| 1185 | 2100 |
| 1197 | 1745 |
| 1211 | 1420 |
| 1226 | 1075 |
| 1242 | 745 |
| 1248 | 650 |
| 1268 | 365 |
| 1277 | 275 |
| 1289 | 235 |
| 1315 | 205 |

TABLE V

Summary of Experimental Viscosity Determinations

| <u>Batch</u> | <u>Temperature at Which Viscosity is Approximately 300 Poises</u> | <u>Batch</u> | <u>Temperature at Which Viscosity is Approximately 300 Poises</u> |
|--------------|---|--------------|---|
| 1 | 1305 | 46 | 1254 |
| 24 | 1450 | 48 | 1110 |
| 25 | 1470 | 49 | 1087 |
| 31 | 1342 | 50 | 1067 |
| 32 | 1455 | 52 | 1088 |
| 41 | 925 | 63-2 | 1269 |
| 43 | 1060 | 64 | 1326 |
| 45 | 1170 | 65 | 1267 |

TABLE VI

Experimental Values - Young's Modulus

| Batch | Number of Samples | Slow Anneal (in Kiln) | Rapid Anneal (in W Furnace) | Average Modulus ($\times 10^5$ kg/cm ²) | Average Modulus ($\times 10^6$ psi) | Maximum Modulus ($\times 10^5$ Kg/cm ²) | Maximum Modulus ($\times 10^6$ psi) |
|------------|-------------------------|-----------------------------|-----------------------------------|--|--|--|--|
| 1 | 10 | x | | 10.46 | 14.86 | 10.82 | 15.43 |
| 4 | 3 | x | | 10.50 | 14.94 | 10.59 | 15.10 |
| 14 | 3 | x | | 10.60 | 15.07 | 10.74 | 15.31 |
| 24 | 9 | x | | 7.51 | 10.67 | 10.68 | 15.22 |
| 26 | 12 | x | | 7.17 | 10.18 | 7.32 | 10.40 |
| 27 | 4 | x | | 8.11 | 11.53 | 8.33 | 11.84 |
| 29 | 12 | x | | 9.86 | 14.02 | 10.68 | 15.22 |
| 41 | 10 | x | | 7.62 | 10.83 | 8.08 | 11.48 |
| 42 | 8 | x | | 7.61 | 10.82 | 7.93 | 11.28 |
| 43 | 20 | x | | 7.23 | 10.27 | 9.10 | 12.93 |
| 45 | 12 | x | | 7.79 | 11.08 | 8.02 | 11.39 |
| 46B | 10 | x | | 7.31 | 10.40 | 7.77 | 11.05 |
| 47 | 9 | x | | 7.78 | 11.07 | 8.49 | 12.07 |
| 48B | 12 | x | | 7.94 | 11.28 | 8.27 | 11.76 |
| 50 | 9 | x | | 7.81 | 11.10 | 8.07 | 11.47 |
| 51 | 8 | x | | 8.26 | 11.75 | 8.39 | 11.93 |
| 52 | 10 | x | | 7.64 | 10.87 | 9.97 | 14.18 |
| 63 | 12 | | x | 10.34 | 14.71 | 11.07 | 15.77 |
| 64 | 5 | x | | 10.96 | 15.57 | 11.8 | 16.82 |
| 64(repeat) | 12 | | x | 10.39 | 14.78 | 11.38 | 16.22 |
| 65 | 8 | x | | 10.69 | 15.20 | 11.28 | 16.07 |
| 66 | 12 | x | | 10.65 | 15.14 | 12.43 | 17.73 |
| 68 | 8 | x | | 10.79 | 15.36 | 12.55 | 17.89 |
| 70 | 9 | x | | 10.72 | 15.23 | 11.08 | 15.78 |

TABLE VII

Typical Variation in Young's Modulus As Determined
Dynamically from Several Samples of A Given Glass

| <u>Specimen</u> | <u>Young's Modulus (pounds/in² x 10⁶)</u> | <u>Specimen</u> | <u>Young's Modulus (pounds/in² x 10⁶)</u> |
|-----------------|---|-----------------|---|
| Batch 30 - #1 | 10.15 | Batch 30 - # 9 | 10.05 |
| Batch 30 - #2 | 10.18 | Batch 30 - #10 | 10.17 |
| Batch 30 - #3 | 10.17 | Batch 30 - #11 | 10.38 |
| Batch 30 - #4 | 10.0 | Batch 30 - #12 | 10.38 |
| Batch 30 - #5 | 10.38 | Batch 31 - # 1 | 11.55 |
| Batch 30 - #6 | 10.35 | Batch 31 - # 2 | 11.45 |
| Batch 30 - #7 | 9.94 | Batch 31 - # 3 | 11.87 |
| Batch 30 - #8 | 10.23 | Batch 31 - # 4 | 11.25 |

TABLE VIII

Comparative Results of Sonic and Transverse Rupture Determinations of
Young's Modulus for Glass #1

| <u>Specimen</u> | <u>Sonic Modulus (pounds/in² x 10⁶)</u> | <u>Transverse Rupture Value (pounds/in² x 10⁶)</u> |
|-------------------|---|--|
| 1 | 14.5 | 13.79 |
| 2 | 14.8 | 14.50 |
| 3 | 15.1 | 14.06 |
| 4 | 15.2 | 14.33 |
| 5 | 14.55 | 13.92 |
| 6 | 15.38 | 13.55 |
| 7 | 14.58 | 13.81 |
| 9 | 15.0 | 13.76 |
| 10 | 14.4 | 13.20 |
| 11 | 15.36 | 14.50 |
| Average | 14.89 | 13.94 |
| Average Deviation | ± 0.32 | ± 0.32 |

TABLE IXA

Calculations of Young's Modulus for Owens-
Corning Experimental Glass OCX-2124 (Ref. 49)

| <u>Constituent</u> | <u>Wt. %</u> | <u>Mole Wt.</u> | <u>Mole Fraction</u> | <u>Mole %</u> | <u>Kilobars/Mole %</u> | <u>Contribution</u> |
|--------------------------------|--------------|-----------------|--------------------------|---------------|------------------------|---------------------|
| SiO ₂ | 71.1 | 60.06 | 1.185 | 70.0 | 7.3 | 511 |
| Al ₂ O ₃ | 21.5 | 101.94 | 0.211 | 12.5 | 12.1 | 151 |
| BeO | 7.4 | 25.02 | 0.296 | 17.4 | X | 17.4X |
| | | | | | | <hr/> 662 + 17.4X |

But Owens-Corning (Ref. 10) achieved 14.4×10^6 psi or 992 kilobars

$$\therefore \text{BeO factor} = \frac{992 - 662}{17.4} = 19.0 \text{ kilobars/mole \%}$$

TABLE IXB

Calculation of Young's Modulus for Example 4,
U. S. Patent 3,127,277 (Ref. 50)

| <u>Constituent</u> | <u>Wt. %</u> | <u>Mole Wt.</u> | <u>Mole Fraction</u> | <u>Mole %</u> | <u>Kilobars/Mole %</u> | <u>Contribution</u> |
|--------------------|--------------|-----------------|----------------------|---------------|------------------------|---------------------|
| SiO ₂ | 51 | 60.06 | 0.850 | 42.5 | 7.3 | 310 |
| CaO | 13 | 56.08 | 0.232 | 11.6 | 12.6 | 146 |
| MgO | 9 | 40.32 | 0.223 | 11.1 | 12.0 | 133 |
| BeO | 11 | 25.02 | 0.440 | 22.0 | X | 22X |
| ZrO ₂ | 2 | 123.22 | 0.016 | 0.8 | 28.6* | 23 |
| TiO ₂ | 8 | 79.90 | 0.100 | 5.0 | 13.3 | 66.5 |
| Li ₂ O | 3 | 29.88 | 0.100 | 5.0 | 7.0 | 35 |
| CeO ₂ | 3 | 172.13 | 0.018 | 0.9 | 13.0 | 12 |
| | | | | | | <u>725.5 + 22X</u> |

*See Table X

But Owens-Corning achieved 16.6×10^6 psi or 1144 kilobars

$$\therefore \text{BeO factor} = \frac{1144 - 725.5}{22} = 19.0 \text{ kilobars/mole \%}$$

TABLE IXC

Calculation of Young's Modulus for Loewenstein's Glass Z_1^1

| <u>Constituent</u> | <u>Wt. %</u> | <u>Mole Wt.</u> | <u>Mole Fraction</u> | <u>Mole %</u> | <u>Kilobars/Mole %</u> | <u>Contribution</u> |
|--------------------------------|--------------|-----------------|----------------------|---------------|------------------------|---------------------|
| SiO ₂ | 50.0 | 60.06 | 0.833 | 50 | 7.3 | 365 |
| Al ₂ O ₃ | 5.0 | 101.94 | 0.049 | 2.93 | 12.1 | 35.4 |
| ZrO ₂ | 12.0 | 123.22 | 0.097 | 5.82 | Y | 5.82Y |
| MgO | 14.0 | 40.32 | 0.347 | 20.82 | 12.0 | 250 |
| CaO | 19.0 | 56.08 | 0.339 | 20.83 | 12.6 | 256 |
| | | | | | | <hr/> 912.2 + 5.82Y |

But Z_1^1 (exp. value) = $11 \times 10^5 \text{ kg/cm}^2 = 1078 \text{ kilobars}$

$$\therefore \text{ZrO}_2 = \frac{166}{5.82} = 28.6 \text{ kilobars/mole \%}$$

TABLE X

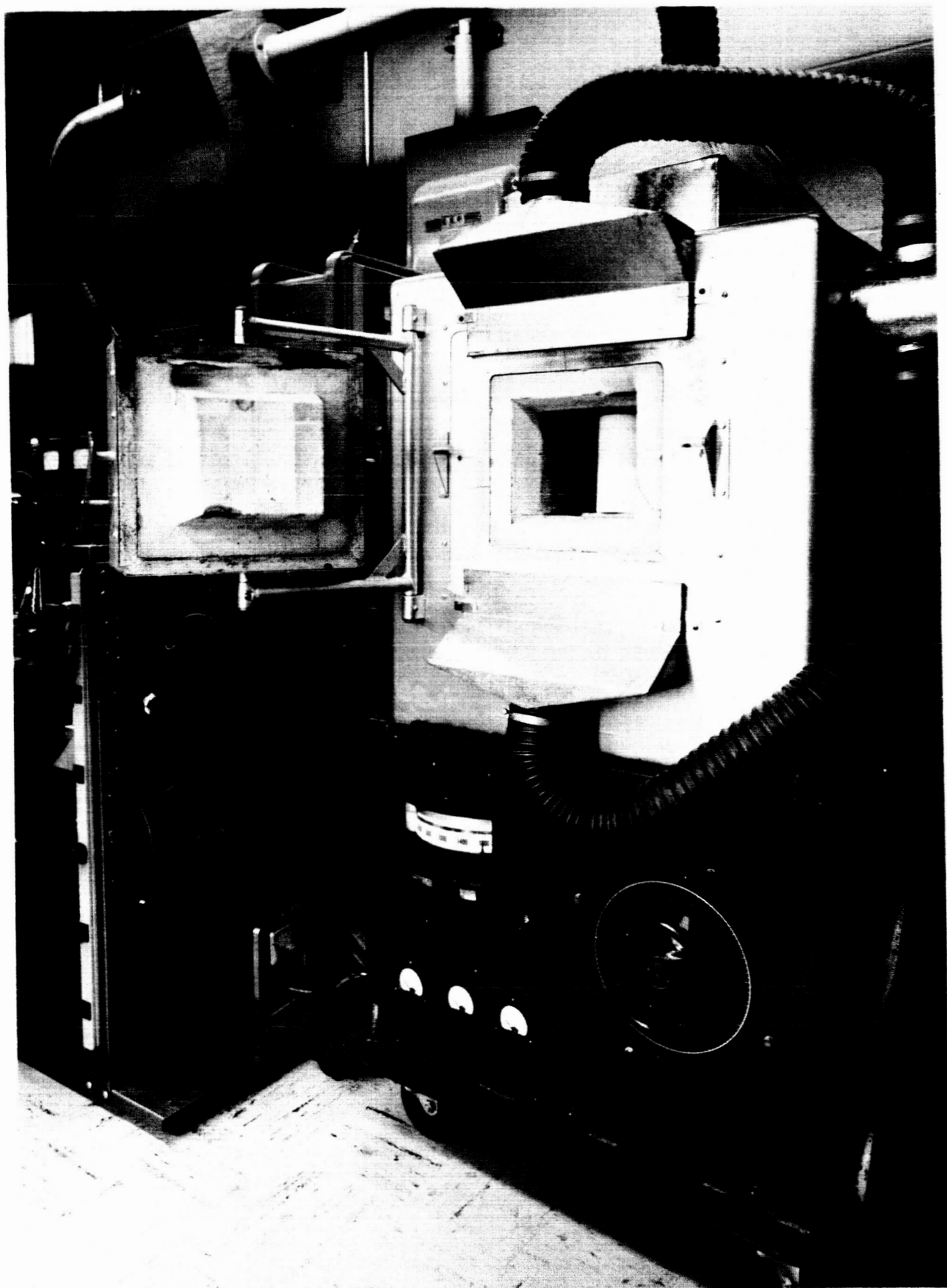
Evaluation of Glass Making Characteristics and
Fiberizability of Some of the
Experimental Compositions

| <u>Melt</u> | <u>Pouring Temp. (°C)</u> | <u>Quality of Glass</u> | <u>Fiberizing Characteristics</u> |
|-------------|-----------------------------------|--|--|
| 1 | ---- | Optical | Not evaluated |
| 2 | ---- | up to 1600 C no evidence of melting | ---- |
| 4 | ---- | Optical | Not evaluated |
| 14 | ---- | Optical | Not evaluated |
| 15 | ---- | Optical, water white | Not evaluated |
| 18 | 1560 | Glassy only in center | Not evaluated |
| 21 | --- | Optical, water white | Not evaluated |
| 22 | 1586 | Cinders only (no apparent melting) | ---- |
| 23 | 1510 & 1574 | No evidence of melting | Not evaluated |
| 24 | ---- | Good | Not evaluated |
| 26 | ---- | Optical - light green color | Not evaluated |
| 27 | ---- | Optical - light blue color | Not evaluated |
| 28 | 1576 | Optical - amber color | Excellent |
| 29 | ---- | Crystalline mass | Not evaluated |
| 30 | ---- | Optical - light green color | Not evaluated |
| 31 | ---- | Optical - light blue color | Not evaluated |
| 36 | 1564 | Could form only a few glass specks | Could not fiberize |
| 37 | 1582 | Optical | Fiber has inclusions and is brittle |
| 39 | 1576 | Optical - lemon color | Excellent |
| 41 | 1588 | Optical | Excellent, glass very fluid |
| 42 | 1202 | Optical | Excellent |
| 43 | ---- | Good | Not evaluated |
| 44 | ---- | Good | Not evaluated |
| 45 | 1592 | Optical | Excellent |
| 46 | ---- | Good | Not evaluated |
| 46B | ---- | Good | Not evaluated |
| 47 | ---- | Good | Not evaluated |

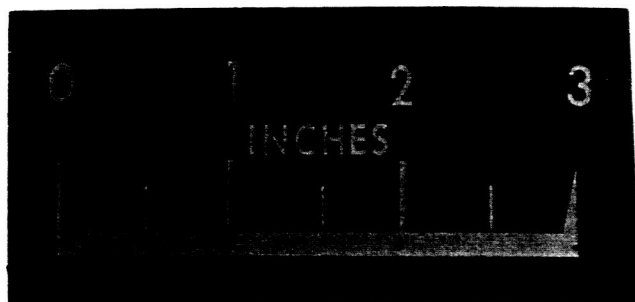
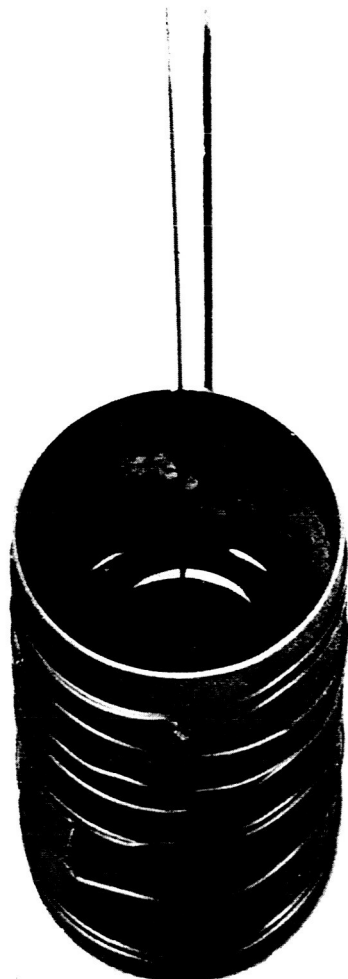
TABLE X (Contd.)

| <u>Melt</u> | <u>Pouring Temp. (°C)</u> | <u>Quality of Glass</u> | <u>Fiberizing Characteristics</u> |
|-------------|-----------------------------------|-------------------------|---------------------------------------|
| 48B | ---- | Good | ---- |
| 50 | 1594 | Optical - light amber | Excellent |
| 51 | ---- | Good glass in center | ---- |
| 52 | ---- | Good | ---- |
| 53 | ---- | Good | ---- |
| 54B | 1582 | Poor | Not readily fiberized |
| 55 | ---- | Optical | Excellent |
| 56 | 1580 | Water white optical | Excellent |
| 59 | 1574 | Optical | Too fluid |
| 60 | 1576 | Optical | Too fluid |
| 61 | 1586 | Optical | Excellent |
| 62 | 1586 | Optical - amber color | Exceptionally well |
| 63 | 1594 | ---- | Will not pour at this temperature |
| 64 | ---- | Optical | Excellent |
| 65 | 1586 | ---- | Will not pour at this temperature |
| 66 | ---- | Optical | Not evaluated |
| 67 | ---- | Optical | Not evaluated |
| 68 | ---- | Optical | ---- |
| 70 | 1600 | Optical - water white | Fine fiberization |
| 71 | 1566 | Optical | Excellent |
| 72 | ---- | Good | Not evaluated |
| 74 | ---- | Good | Not evaluated |
| 75 | ---- | Good | Not evaluated |

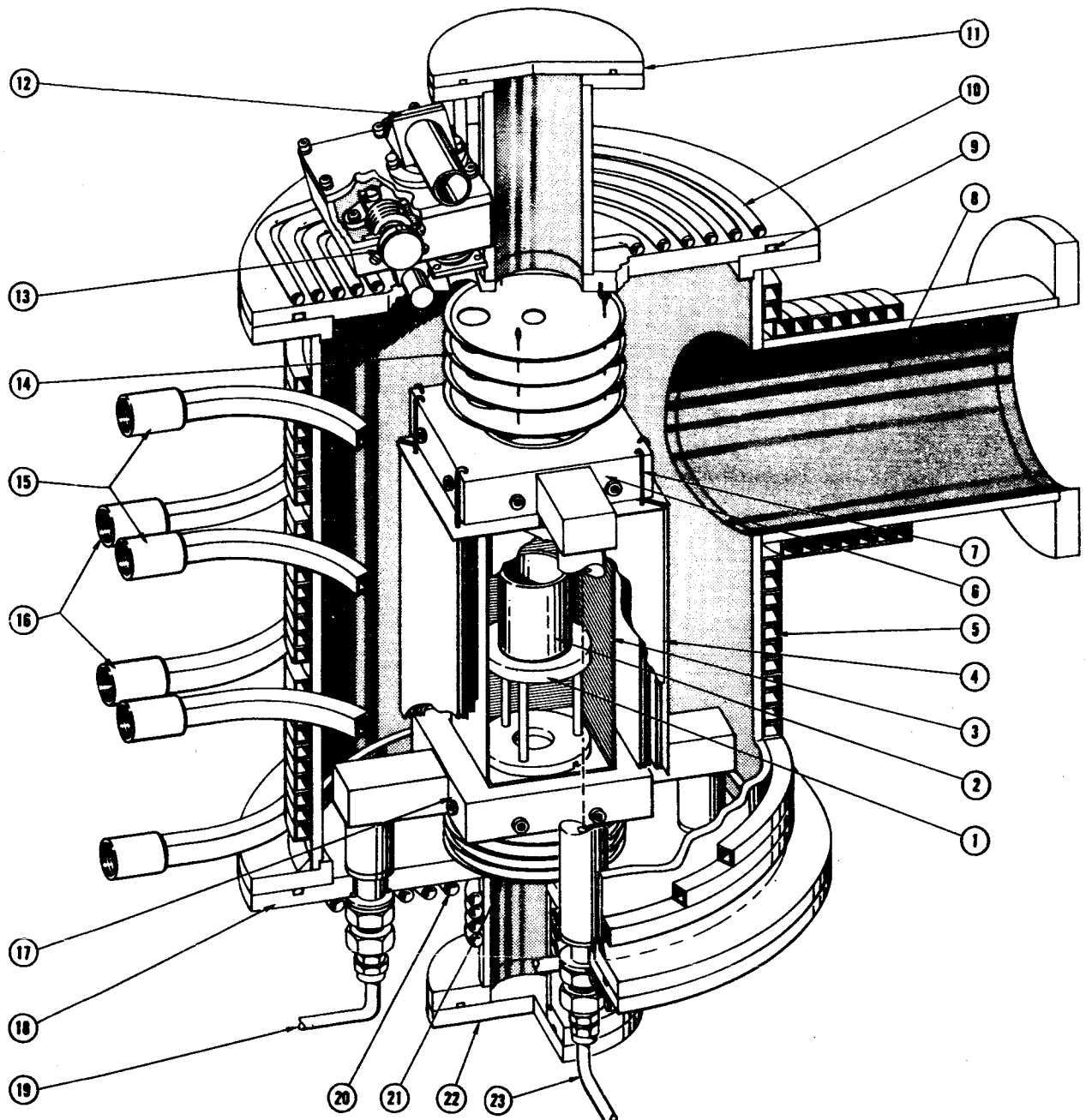
SUPER-KANTHAL HAIR-PIN KILN USED FOR
MELTING OXIDE MIXTURES



TUNGSTEN CRUCIBLE CONDUCTIVITY CELL



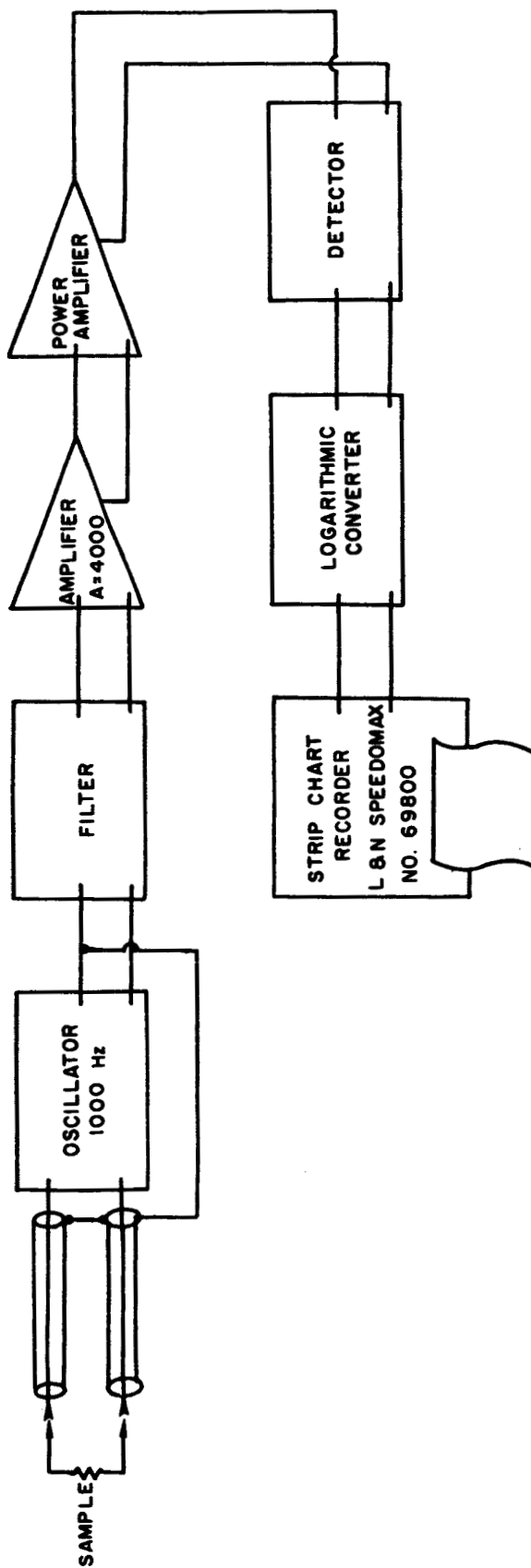
HIGH TEMPERATURE TUNGSTEN RESISTANCE FURNACE



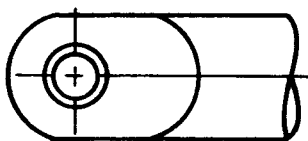
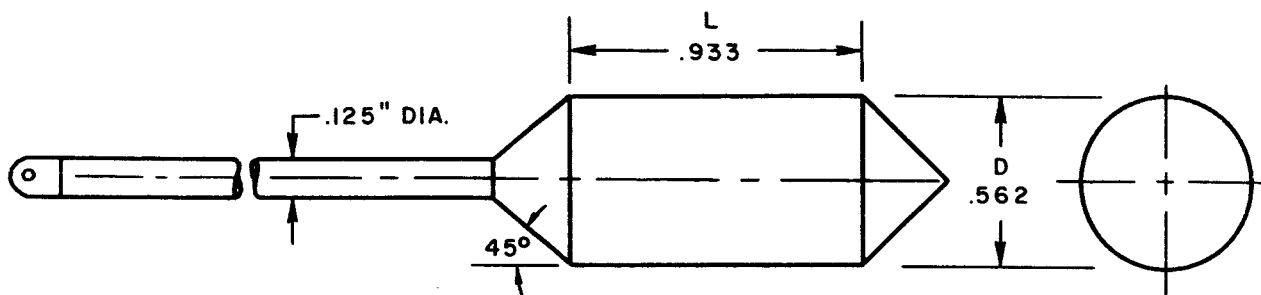
- ① TUNGSTEN PEDESTAL FOR CRUCIBLE
- ② TUNGSTEN CRUCIBLE
- ③ FLAT TUNGSTEN HEATING ELEMENT (4)
- ④ TANTALUM RADIATION SHIELDS
- ⑤ SIDE COPPER COOLING COILS
- ⑥ TOP WATER COOLED ELECTRODE SUPPORT CONDUCTOR
- ⑦ SUPPORT PIN FOR TANTALUM SHIELDS
- ⑧ TO VACUUM SYSTEM
- ⑨ "O" RING GASKET SEALS
- ⑩ TOP COPPER COOLING COILS
- ⑪ TOP INTERCHANGABLE COVER FOR MEASURING APPARATUS
- ⑫ SIGHT GLASS

- ⑬ PROTECTOR MECHANISM FOR SIGHT GLASS
- ⑭ TOP TANTALUM RADIATION SHIELDS
- ⑮ COOLING WATER IN
- ⑯ COOLING WATER OUT
- ⑰ BOTTOM WATER COOLED ELECTRODE SUPPORT CONDUCTOR
- ⑱ BOTTOM PLATE FOR MOUNTING
- ⑲ WATER IN BOTTOM ELECTRODE
- ⑳ BOTTOM COPPER COOLING COILS
- ㉑ BOTTOM TANTALUM RADIATION SHIELDS
- ㉒ BOTTOM INTERCHANGABLE COVER FOR MEASURING APPARATUS
- ㉓ WATER IN TOP ELECTRODE

LOG OHMMETER



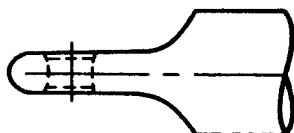
LARGE TUNGSTEN SPINDLE USED FOR HIGH TEMPERATURE VISCOSITY MEASUREMENT



BROOKFIELD VISCOMETER MODEL: RVT

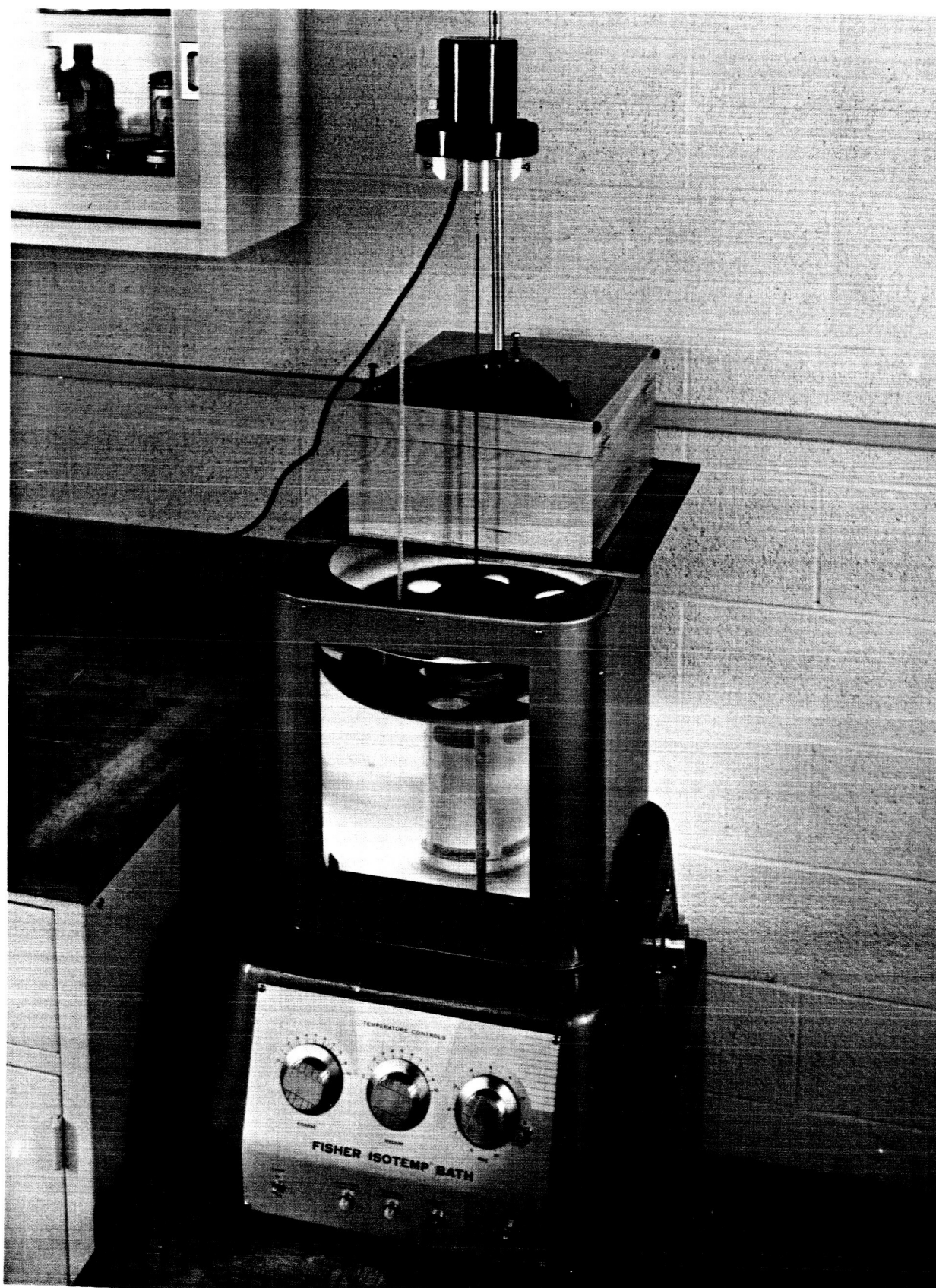
CONTAINER DIAMETER: 2"

MINIMUM CONTAINER DEPTH: 2"

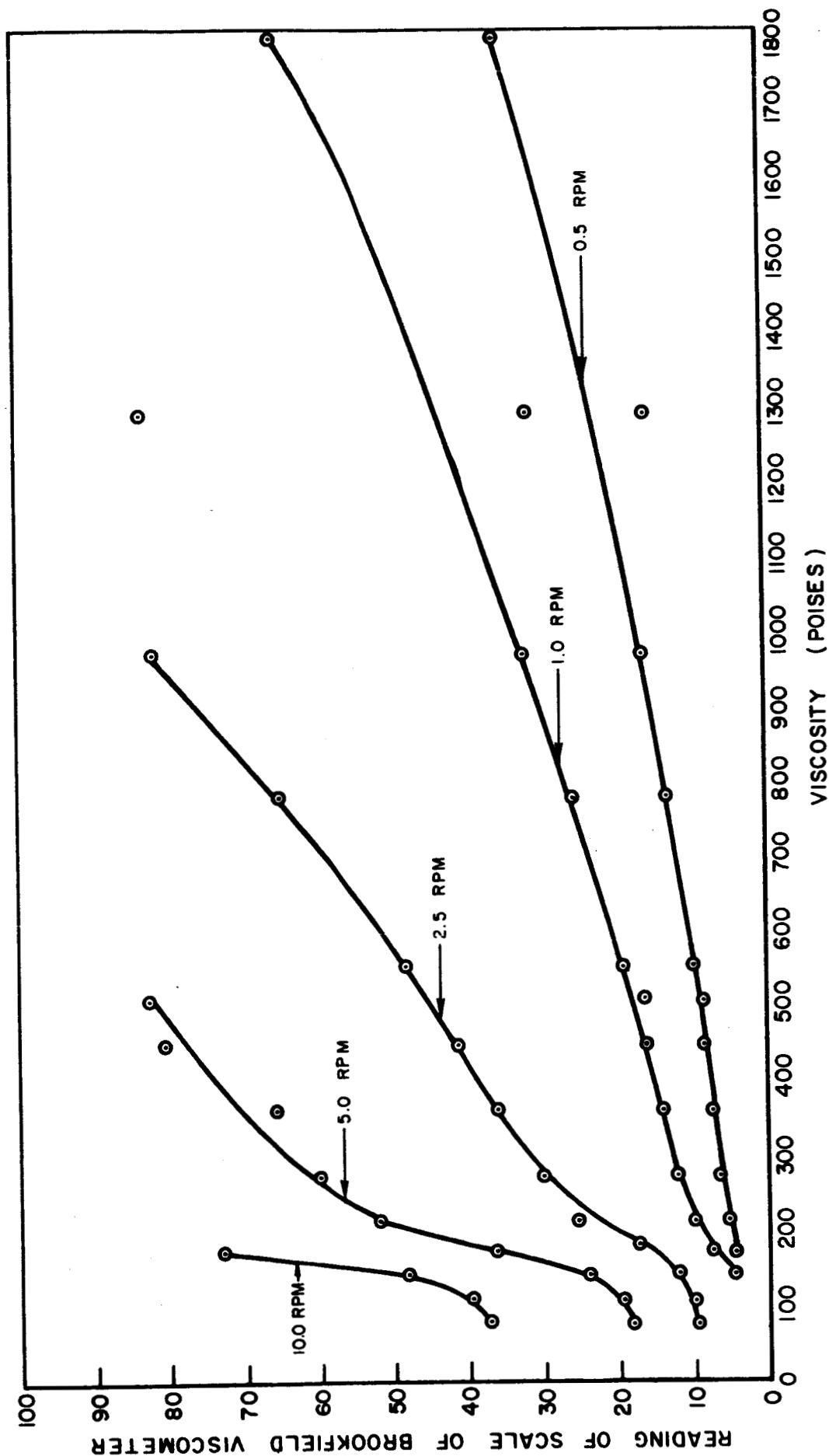


| <u>SPEED (R.P.M.)</u> | <u>RANGE (CPS)</u> |
|-----------------------|--------------------|
| 100 | 0 - 3000 |
| 50 | 6000 |
| 20 | 15,000 |
| 10 | 30,000 |
| 5 | 60,000 |
| 2.5 | 120,000 |
| 1 | 150,000 |
| 0.5 | 600,000 |

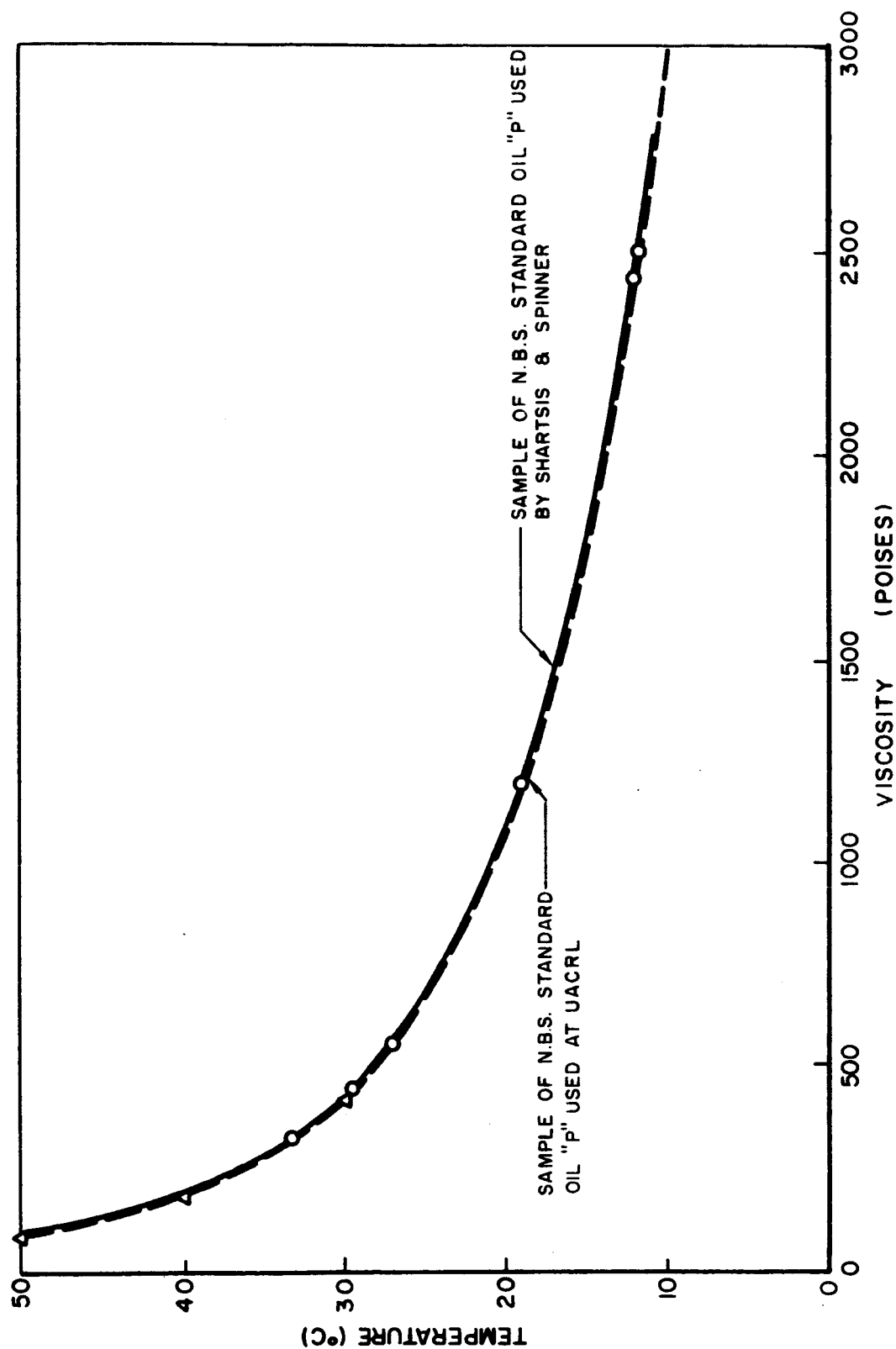
BROOKFIELD VISCOMETER AND CONSTANT TEMPERATURE
BATH USED FOR CALIBRATION



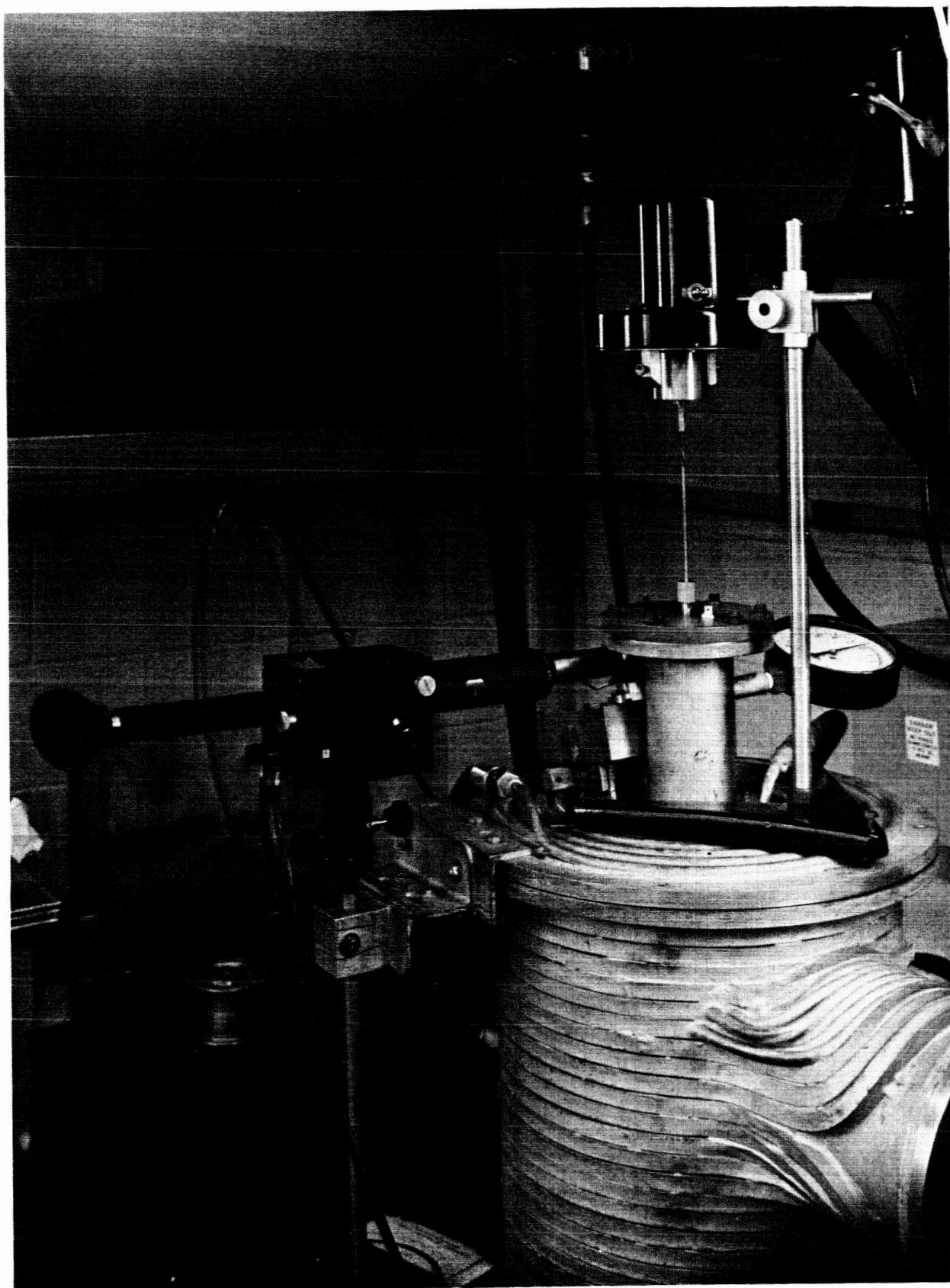
CALIBRATION DATA FOR LARGE TUNGSTEN SPINDLE, BROOKFIELD VISCOMETER, AND STANDARD OIL "P" FROM N.B.S.



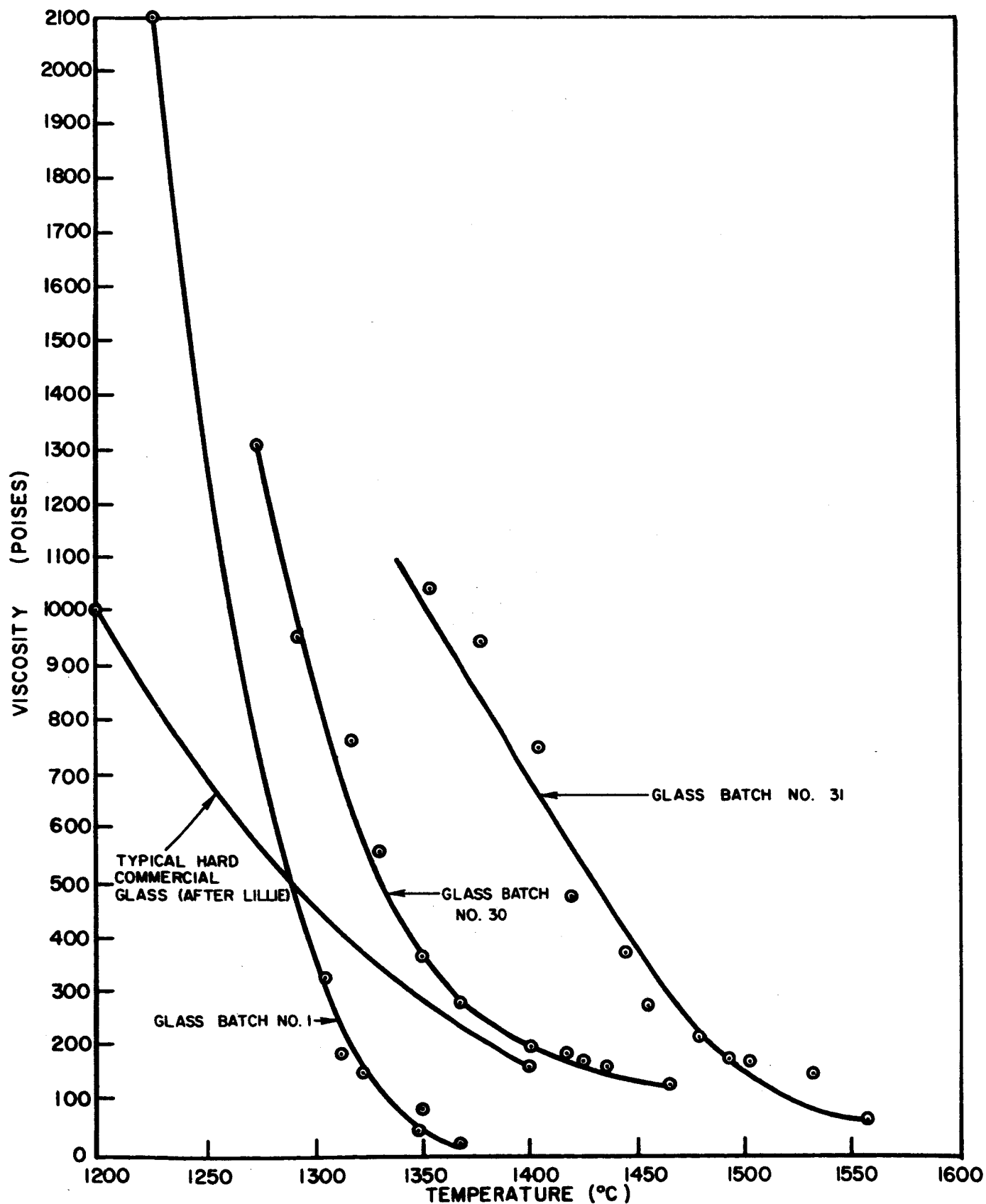
EXTRAPOLATED CALIBRATION CURVE FOR N.B.S. VISCOSITY STANDARD "P"



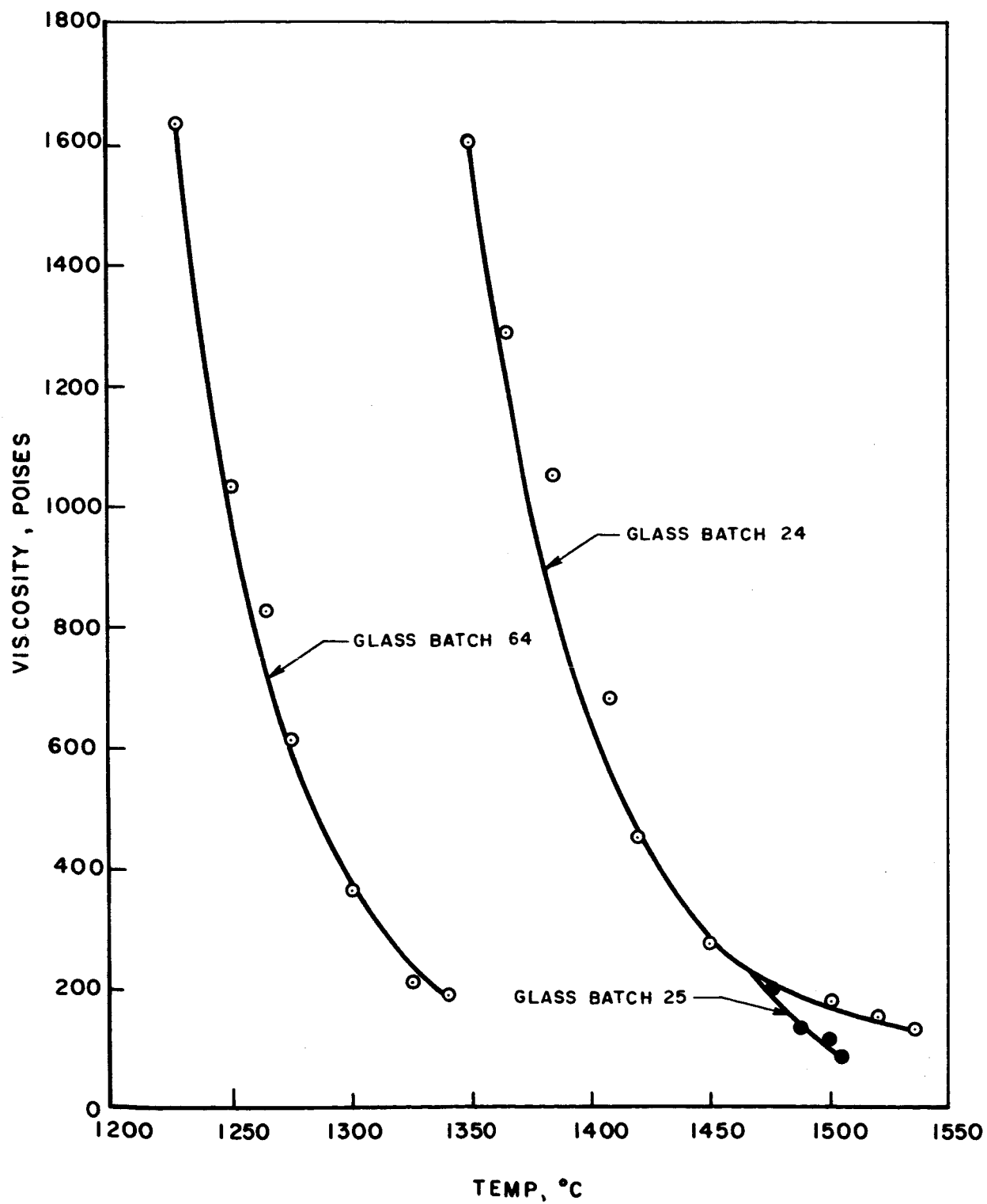
BROOKFIELD VISCOMETER INSTALLED ON TUNGSTEN FURNACE
FOR HIGH TEMPERATURE VISCOSITY MEASUREMENTS



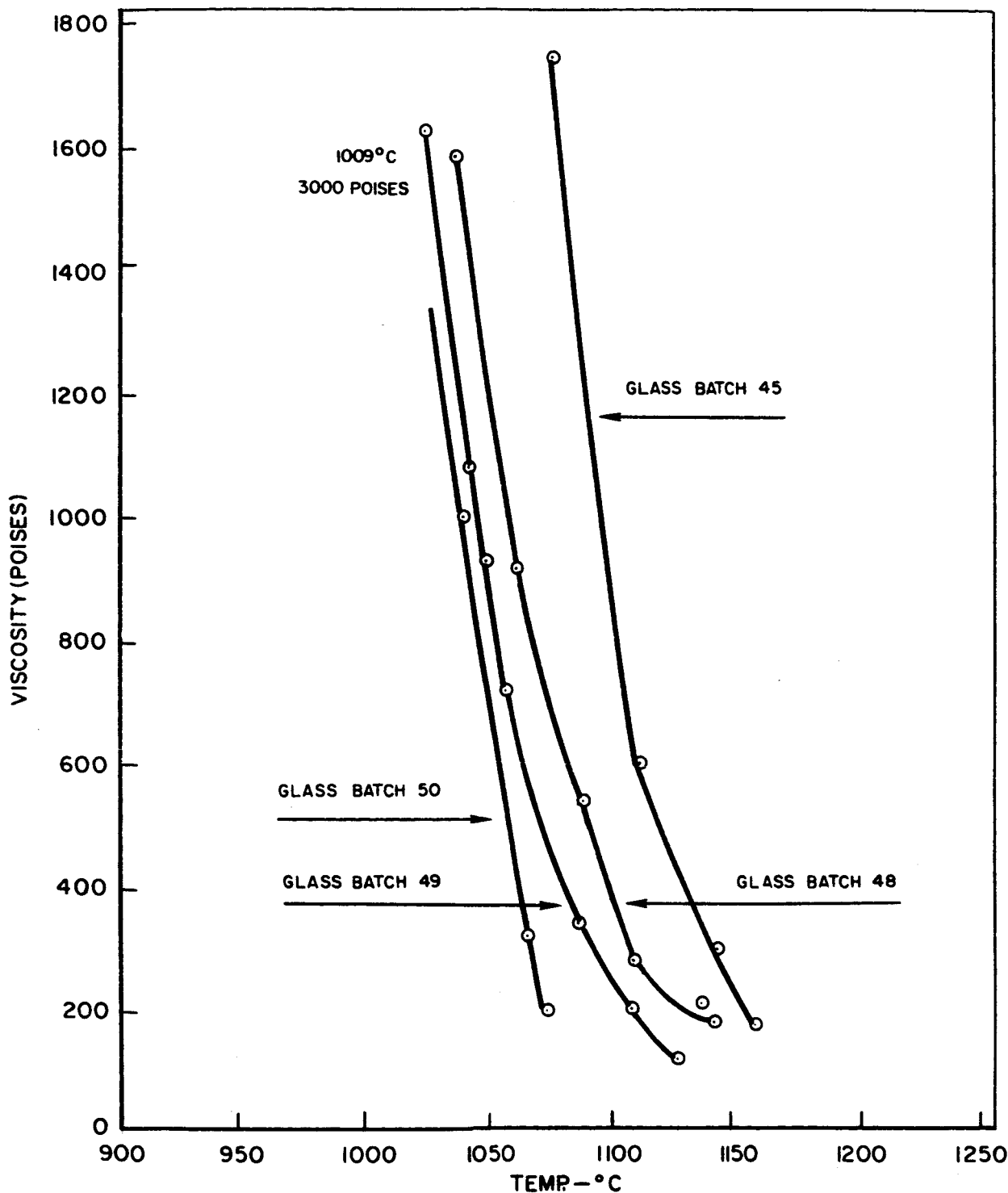
EXPERIMENTALLY DETERMINED VISCOSITY-TEMPERATURE RELATIONS



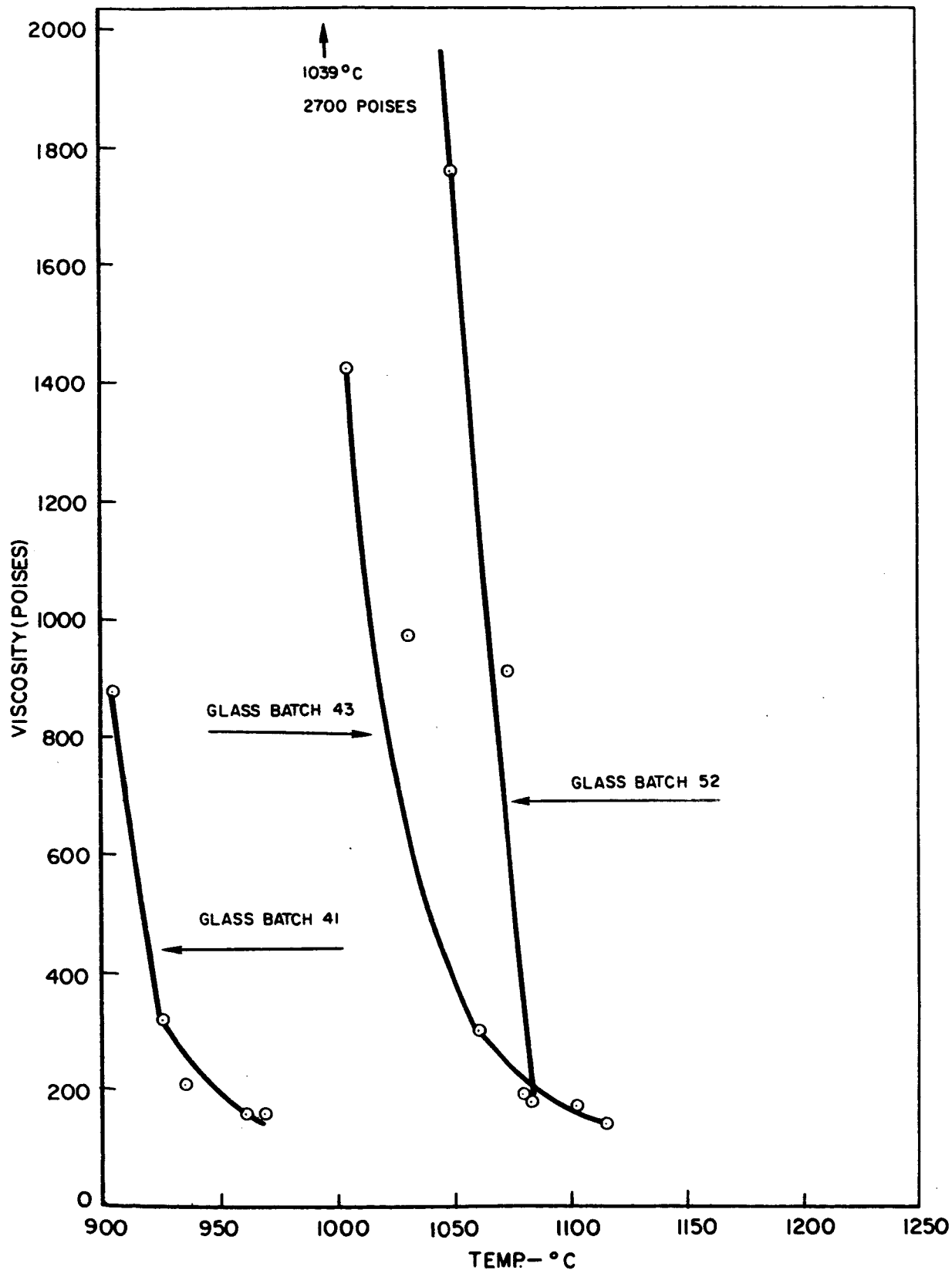
EXPERIMENTALLY DETERMINED VISCOSITY-TEMPERATURE RELATIONS



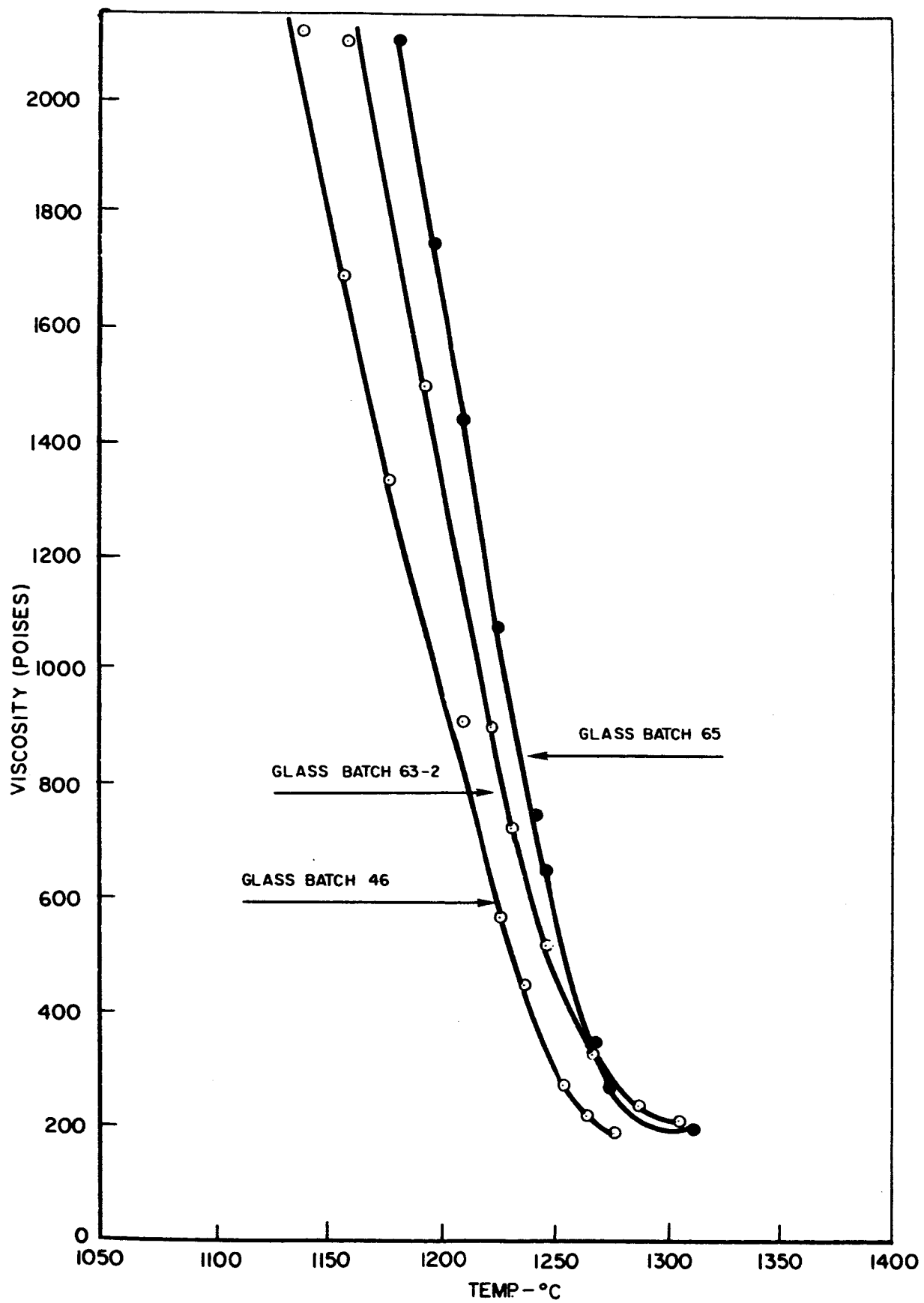
EXPERIMENTALLY DETERMINED VISCOSITY-TEMPERATURE RELATIONS



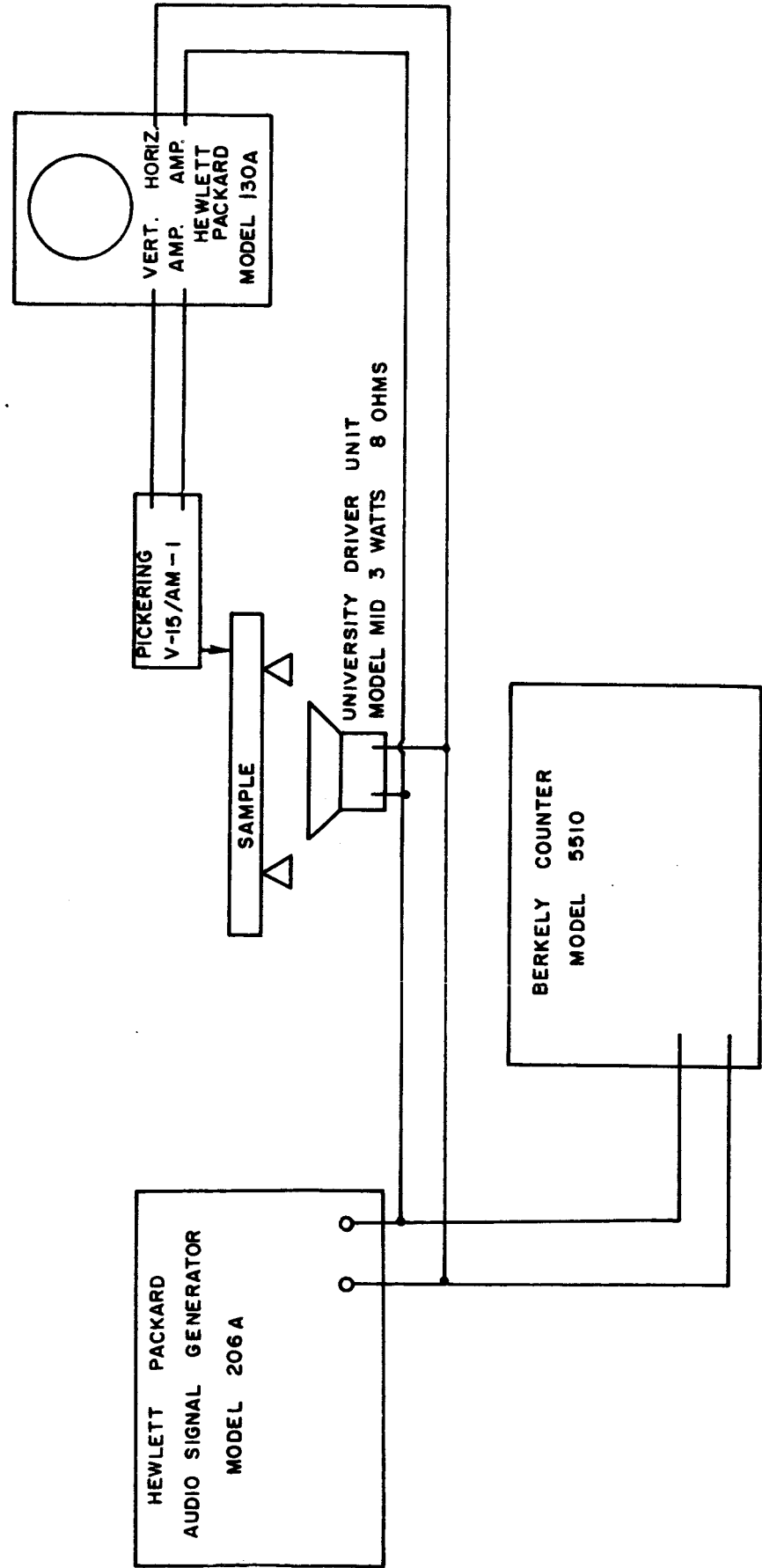
EXPERIMENTALLY DETERMINED VISCOSITY-TEMPERATURE RELATIONS



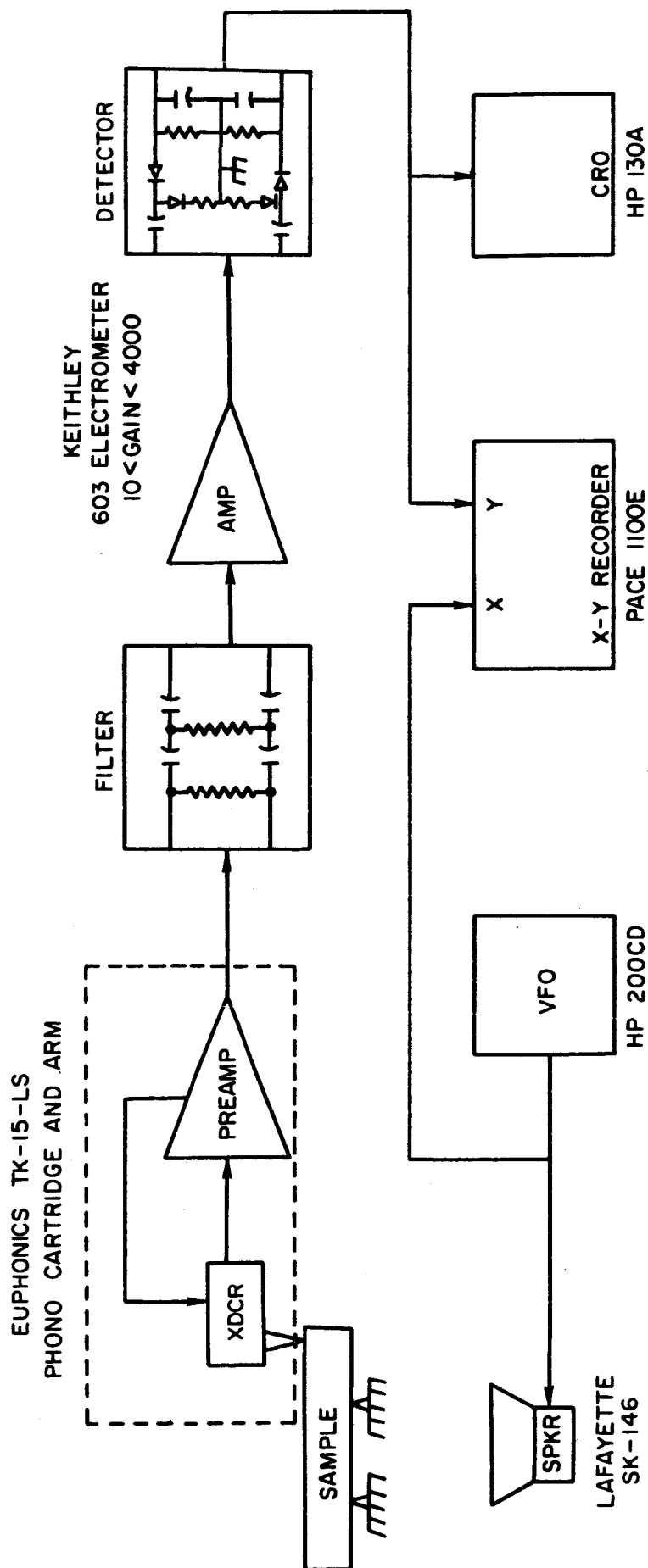
EXPERIMENTALLY DETERMINED VISCOSITY-TEMPERATURE RELATIONS



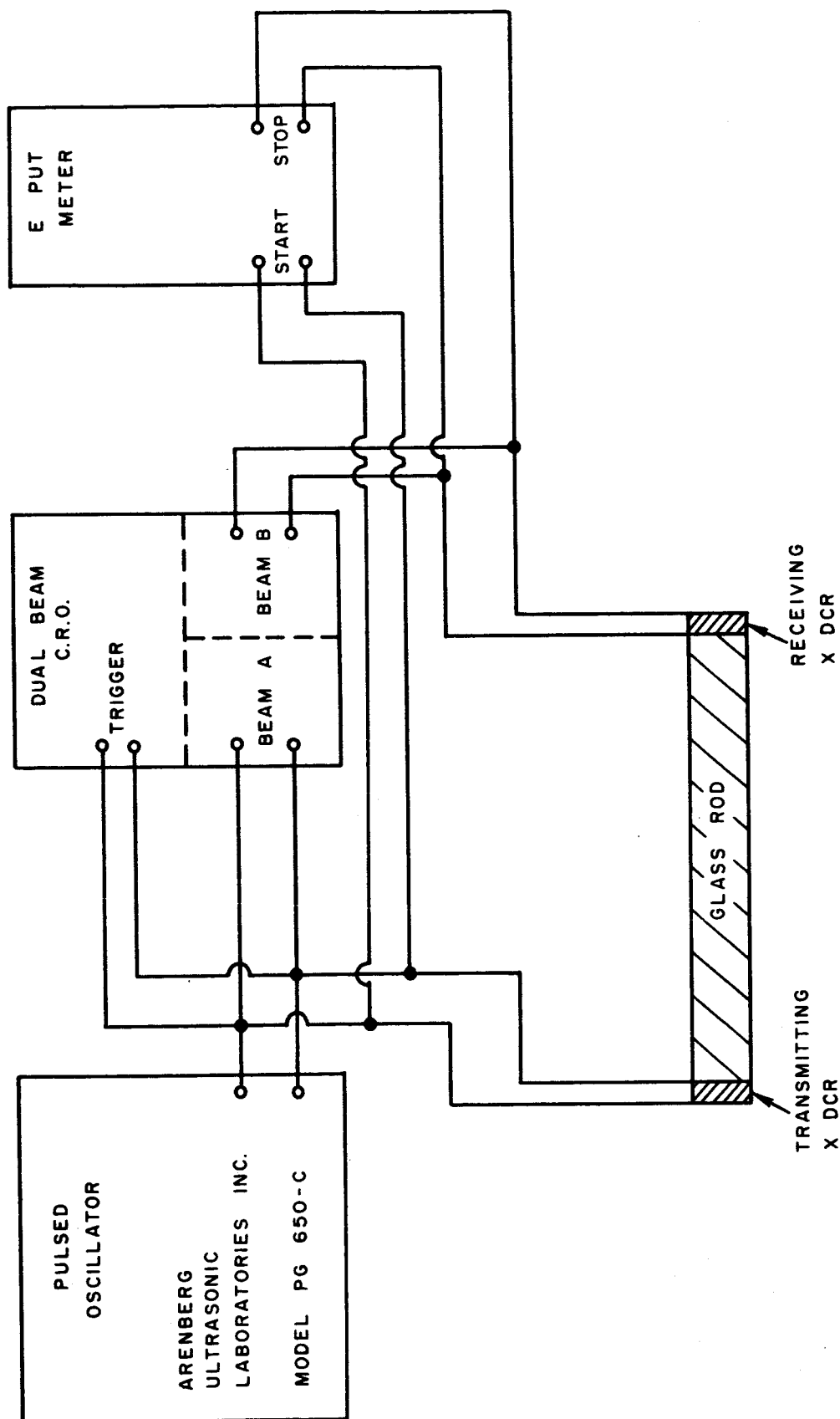
SONIC EQUIPMENT ASSEMBLED FOR MEASUREMENT OF YOUNG'S MODULUS



IMPROVED APPARATUS USED FOR THE MEASUREMENT OF YOUNG'S MODULUS



APPARATUS FOR DETERMINING SHEAR MODULUS BY MEASUREMENT OF THE VELOCITY OF SOUND



PLATFORM KILN USED FOR FIBERIZABILITY STUDIES

